

POLLUTION PREVENTION AND INSTITUTIONAL INCINERATION

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The Clean Combustion Technology Laboratory (CCTL) has conducted pilot scale experiments since December 1987 on precombustion and combustion techniques for reducing organic emissions from an institutional incinerator. Using hydrogen chloride (HCl) and volatile organic compound (VOC) sampling methods, we have correlated stack emissions with characteristic inputs and combustion conditions. Our experimental results indicate that avoidance of and source separation of chlorinated wastes, burning slightly above stoichiometric, and stoking the waste bed are effective methods of minimizing toxic emissions. By these measures we have already achieved equivalent HCl and VOC scrubbing of approximately 90% without post combustion measures and believe we can do better. Phenomenological and kinetic modeling of data in the literature supports this approach to toxic minimization. We propose simple measures for transferring the benefits of this institutional approach to community waste problems.

INTRODUCTION

Title III of the Clean Air Act Amendments of 1990 defines 189 toxic chemicals and 250 source categories

which will come under regulatory constraints at various times in the 1990s. It will require considerable measurements of toxic emissions of waste, biomass, coal and combinations of solid fuels under various combustion conditions to assess the impact of this legislation on waste to energy system. The Clean Combustion Technology Laboratory (CCTL) has been engaged in the measurement and minimization of toxic products of institutional waste incineration since 1988. This work is a continuation of our studies on co-combustion of fuels which began in 1980 on a laboratory scale and in 1985 on an institutional or industrial scale [1-12]. Our incinerator facilities at Tacachale (formerly named Sunland at Gainesville) include a 500 lb/hr (227 kg/h) Environmental Control Products (ECP) incinerator, the primary facility used in our toxics measurement program. The incinerator, the stack sampling configuration and the instrumentation have been described in our recent papers [9, 10, 12]. This measurement and toxics minimization program has involved the combustion of non-hazardous (NHW) and co-combustion of NHW, cellulosic biomass (CB), and coal (C) together with natural gas (NG). Results which have already been published [9-12] are summarized in the sections on Hydrogen Chloride Emissions and Chlorinated Organic Emissions.

HYDROGEN CHLORIDE EMISSIONS

Hydrogen chloride (HCl) emissions are important corrosive and toxic emissions from municipal and institutional (particularly medical) waste incinerators. Chlorine input in the form of chlorinated organics or chlorides in the waste stream emerge primarily as HCl emissions. HCl emissions tend to reduce the useful lifetime of boilers, induced draft fans, and other post-combustion components. HCl produces lung and eye irritation and contributes to acid deposition in forests, lakes and rivers. Hydrogen chloride is a particular problem with uncontrolled house fires and along with carbon monoxide and hydrogen cyanide, is a leading cause of death due to fires. Chlorinated plastics are significant contributors to HCl emissions from incinerators, particularly medical waste incinerators. However, the correlation of HCl emissions with polyvinylchloride (PVC) input has been obfuscated in some reports [13, 14]. The confusion has largely been based upon ambiguous interpretations of the results of the Vicon study [15] conducted in Pittsfield, Massachusetts using 120 ton/day (109 metric ton/day) incinerators. However a much larger body of scientific literature [16-22] support the almost obvious conclusion that organically bound chlorine in the waste input mostly ends up as hydrogen chloride (HCl).

In view of the confusion as to the relationship between PVC input and HCl output, the CCTL has made a particular effort to experimentally establish this relationship. These experiments were first carried out by feeding measured weights of broken PVC pipe through the biomass feeding port in the incinerator [10]. In our most recent experiments we used measured weights of PVC resin. Both sets of measurements support the conclusion that HCl emissions are related linearly to chlorine (PVC) input. Our data from 22 HCl measurements (11 with PVC spiking) using a draft EPA method [23] when scaled to a standard 400 lb/hr (182 kg/h) NHW input lead to the linear relationship [12]

$$\text{HCl} = a \text{ Cl} + b \quad (1)$$

where HCl = hydrogen chloride output (lb/hr = 0.454 kg/h) Cl = chlorine input from PVC (in lb/hr), $a = 0.7$ and $b = 1.0$ lb/hr. The constant term $b = 1$ lb/hr or 0.25% probably reflects the amount of chlorine originally present in the waste apart from PVC spiking. The expected slope of the HCl vs. Cl curve should be about 1.0 rather than 0.7. Solubility of HCl in water and other problems in the measurement methodology and the unknown purity of the broken PVC pipe probably account for the discrepancy.

TABLE 1 COMPARISON OF RESULTS FROM CARB VOLATILE ORGANIC SAMPLING TO CCTL SAMPLING

Compound	California Hospital Average	CCTL Non-spiked Average	CCTL PVC spiked Average	CCTL/Cal Effective Scrubbing Efficiency
(µg/dscm @ 7% O ₂)				
1,2-dichloroethane	81.3	0.0	0.0	100%
1,1,1-trichloroethane	73.0	1.7	1.7	98%
Carbon tetrachloride	3.3	2.2	3.6	33%
Trichloroethene	26.9	0.2	0.6	99%
Tetrachloroethene	37.5	0.2	0.3	99%
Chloroform	2.0	1.9	7.7	3%
Benzene	11470.5	17.3	49.5	100%
Toluene	87.8	15.5	11.1	82%
Ethylbenzene	21.4	2.6	4.5	88%
m,p-Xylene	205.9	2.3	2.0	99%
o-Xylene	27.4	0.6	0.7	98%

CHLORINATED ORGANIC EMISSIONS

For about 3 years we have had an operational Method 5 sampling train for particulates [24] and for about 2 years a volatile organic sampling train (VOST) [25]. These have given consistent results which have been reported in our recent publications [9, 10, 12]. We also have built up a modified method five (MM5) sampling train for semi-volatiles [26]. Here, however, we have not yet achieved quantitative results. A major problem is the long sampling times needed for good GC/MS analyses. Sampling times of 6 hr or greater are difficult with our current overall waste collection and combustion procedures. In contrast our VOST sampling typically requires only 20 min to obtain a sample for GC/MS analysis.

We have recently compared our volatile organics with corresponding concentrations given in reports of the California Air Resources Board (CARB) on medical incinerators without post combustion controls [27]. Table 1 recapitulates these comparisons. Note that in all cases the concentrations in our stack gases are substantially lower than the average concentrations of the same VOC measured by CARB when normalized to the same O₂ concentrations.

Table 1 also shows a comparison of averages of emissions of volatile chlorinated hydrocarbons when burning nonhazardous waste (NHW) with emissions from burning PVC-spiked NHW. Note the large increase in the emission of several compounds, particularly carbon tetrachloride, chlorobenzene, chloroform, and dichlorobenzene. Emissions of nonchlorinated volatile aromatics (except benzene) stayed about the same. This suggests that the addition of PVC to the waste stream leads to increased emission of other chlorinated hydrocarbons, such as phenols, dioxins, and furans. Volatile chlorinated hydrocarbons emissions from coburning NHW, biomass, and coal were similar to those from

straight NHW burning, while nonchlorinated volatile aromatic emissions increased. We attribute the lower toxic emissions indicated in the CCTL columns of Table 1 to:

(a) our retrofit measures: (1) installations of a stoker; (2) the incorporation of a strong blower for extra underfire air; (3) the installation of an extra tangentially directed overfire air blower (originally for use as a inducing agent for our biomass feeder); (4) our operational protocol of running at higher temperatures (1800°F primary, 2000°F secondary) rather than those of conventional starved air incinerators (1400°F primary, 1700°F secondary).

(b) our protocols of separating: (1) toxics and recyclables and bagging only nonhazardous waste; and (2) avoidance of chlorinated plastics by the Tacachale purchasing agent. This second measure particularly explains our lower HCl levels and further assists in lowering chlorinated organic emissions.

PHENOMENOLOGICAL MODELS OF CHLORINATED HYDROCARBON EMISSIONS

We have noted the limitations of our results on semi-volatile organic emissions using the Modified Method 5 (MMR) sampling train. To compensate for this we have attempted to develop phenomenological models which organize emission data already in the literature. The best set of controlled experiments with a modular incinerator, to our knowledge, are those carried out at the Vicon-Pittsfield incinerator with the support of the New York State Energy Research and Development Authority [15]. The Midwest Research Institute (MRI) has attempted to organize the Vicon Pittsfield incinerator emissions by linear regression analysis [15]. These results indicated strong correlations between some measured variables and weak and nonsignificant correlations between others. Green, Wagner and Lin [11] have reexamined the Vicon data seeking nonlinear relationships between the various measurables. Their one-dimensional (1-D) model related chlorinated hydrocarbon emissions to HCl emissions as a power law which may be expressed in the form

$$Y_i = M_i(X/X_u)^{n_i} = \alpha_i^2 (X/X_u)^{n_i} \quad (2)$$

Here $Y_1 = \text{PCDF} = F$, $Y_2 = \text{PCDD} = D$, $Y_3 = \text{ClBz} = B$, $Y_4 = \text{ClPh} = P$, X is the HCl concentration and X_u is a convenient unit. The parameters M_i and n_i obtained by least square minimization are given in reference [11]. These functions, when examined in rela-

tionship to the data are not very impressive. However, most of the relationships between Y_i 's derived from Eq. (2) by eliminating HCl are quite impressive [10,11]. This observation led us to seek more refined empirical equations to fit the Vicon data. In this pursuit [10, 11, 12] we have examined various two-dimensional (2-D) $Y_i(\text{HCl}, T)$ and three-dimensional (3-D) $Y_i(\text{HCl}, T, \text{CO})$ functions where T is the temperature and CO the carbon monoxide concentration at the tertiary duct. Among approximately 50 analytic functions examined the best to date is the expression (Model 41)

$$Y_i = \alpha_i^2 X \exp n_i X + \beta_i^2 X [\exp m_i X] F(t, \mu, P_i) W^{q_i} \quad (3)$$

where $W = \text{CO}/10$, $t = (T + 460)/100$ and $F(t : p, \mu)$ is an Arrhenius reaction rate type function of the form

$$F(t; p, \mu) = A t^\mu \exp - (p/t) = A_o (t/2)^\mu \exp [(p/2) - (p/t)] \quad (4)$$

In the second form t is normalized by a median value $t = 2$ which makes the amplitude factor A_o relatively insensitive to variations of the Arrhenius parameters p and μ .

A serious problem in phenomenological modeling of the stack emission measurements is the general noisiness of data when the species concentrations are in the parts per billion or parts per trillion level. For example, pairs of Vicon measurements which were supposed to represent duplicate conditions sometimes differ by an order of magnitude. To smooth over this difficulty, in a previous study [12] all Vicon pairs were replaced by the geometric average of the pair. This procedure was used for all pairs of independent variables (X , T , W), as well as the dependent variables $Y_1 = F = \text{PCDF}$, $Y_2 = D = \text{PCDD}$, $Y_3 = B = \text{ClBz}$, and $Y_4 = P = \text{ClPh}$. Using this data we determined the best parameters in Eq. (3) by least square adjustment to the data. Having found good parameter sets to fit geometrically averaged data we return in the present work to the original tertiary duct data.

Table 2(a) gives the original data extracted from the Vicon report [15]. The labels a , c , $d \dots$ denote pairs of data sets which were intended to represent duplicate conditions. The case b is a single set. We use vertical lines to annotate cases within such pairs where the data differs by large factors. Table 2(b) gives the best fit parameters as determined by a nonlinear least square minimization program. Shown also are the uncertainty in these parameters and the chi squares. We have used the restrictions $n = 0$ and $\mu = 1$ to reduce the free parameters and to help seek out patterns in the five

TABLE 2(a) INDEPENDENT AND DEPENDENT VARIABLES

Run No.	Test Condition	HCl kg/t	T °F	CO ppm	PCDF ug/t	PCDD ug/t	ClBz mg/t	ClPh mg/t
a	11 MSW	3.40	1327	152	380	160	2.5	11.0
	22	3.21	1283	251	630	220	7.9	6.2
b	28 MSW	3.01	1458	43	68	15	1.2	4.4
c	10 MSW	2.85	1539	8	49	18	1.5	32.0
	16	3.67	1636	11	71	11	1.6	5.2
d	15 MSW wet w/rain	1.88	1643	8	87	27	7.9	5.2
	21 MSW + H ₂ O	3.99	1508	25	200	110	3.6	3.9
f	23 MSW - low O ₂	13.79	1933	3	340	100	4.6	6.4
	26	2.67	1834	12	130	44	1.1	3.0
h	12 PVC-free	0.52	1796	0.5	51	12	5.6	14.0
	17	0.46	1861	2	220	11	2.2	6.9
i	13 PVC-free + PVC	2.57	1739	4	68	30	2.8	9.8
	19	2.10	1840	7	52	27	1.2	4.4
j	24 PVC-free + H ₂ O	0.90	1810	11	450	110	3.6	4.5
	29	1.15	1739	6	74	50	1.1	2.3

TABLE 2(b) BEST FIT PARAMETERS ($n = 0, u = 1$)

	Y ₁ =F=PCDF	Y ₂ =D=PCDD	Y ₃ =B=ClBz	Y ₄ =P=ClPh
alpha	5.012 ± 0.370	2.783 ± 0.274	0.594 ± 0.084	0.453 ± 0.586
beta	43.290 ± 23.962	11.175 ± 6.070	9.364 ± 4.136	2.528 ± 0.318
m	-2.079 ± 0.439	-1.368 ± 0.311	-1.756 ± 0.473	0.007 ± 0.102
p	3.654 ± 13.006	13.693 ± 14.545	-34.872 ± 9.293	-66.070 ± 16.331
q	1.464 ± 0.375	1.511 ± 0.527	-0.208 ± 0.186	-1.753 ± 0.353
chi ²	61778.2	10031.9	41.9	169.0

TABLE 2(c) CALCULATED VALUES AND ERRORS

	Y ₁ =F=PCDF		Y ₂ =D=PCDD		Y ₃ =B=ClBz		Y ₄ =P=ClPh	
	FIT	ERR	FIT	ERR	FIT	ERR	FIT	ERR
a	294.9	-85.1	124.4	-35.6	4.3	1.8	9.4	-1.6
	647.5	17.5	230.8	10.8	7.0	-0.9	9.1	2.9
b	156.7	88.7	63.1	48.1	3.1	1.9	6.6	2.2
c	81.9	32.9	27.2	9.2	2.8	1.3	28.5	-3.5
	96.6	25.6	33.4	22.4	1.5	-0.07	5.5	0.3
d	105.9	18.9	33.4	6.4	3.5	-4.4	4.1	-1.1
	107.1	-92.9	38.4	-71.6	1.8	-1.8	9.7	5.8
f	346.5	6.5	106.8	6.8	4.9	0.3	7.1	0.7
	103.9	-26.1	52.1	8.1	1.2	0.1	0.8	-2.2
h	18.8	-32.2	4.9	-7.1	5.5	-0.1	17.0	3.0
	58.5	-161.5	11.6	0.6	2.8	0.6	0.7	-6.2
i	72.4	4.4	24.8	-5.2	1.6	-1.2	5.1	-4.7
	96.0	44.6	40.6	13.6	1.3	0.1	0.8	-3.6
j	443.7	-6.3	104.1	-5.9	2.6	-1.0	0.3	-4.2
	150.0	76.0	37.0	-13.0	3.8	2.7	1.2	-1.1

TABLE 2(d) OTHER POTENTIAL VARIABLES

	%H ₂ O in waste	Cl kg/t in waste	%O ₂ at tert duct	PCDF ug/t in waste	PCDD ug/t in waste
a	19.32	0.280	12.8	1624	13671
	16.91	0.132	12.9	408	4218
b	15.73	0.140	11.5	770	4832
	42.96	0.137	10.2	435	1170
c	30.41	0.148	9.2	1243	8673
	50.33	0.062	8.7	481	2658
d	45.58	0.111	10.6	327	2703
	14.37	0.177	4.8	626	426
f	33.75	0.241	4.7	771	1833
	8.76	0.067	7.3	89276*	2549
h	18.66	0.027	7.3	4064	36714*
	21.90	0.335	8.6	1506	10215
i	9.24	0.322	8.4	263	853
	30.87	0.037	7.0	435	4110
j	36.02	0.077	8.0	272	1279

residual parameters. The only obvious pattern which emerges is that $\beta > \alpha$ in all cases. Nevertheless the first term in Eq. (3) cannot be ignored without seriously degrading the fit. Table 2(c) gives the calculated values and the error in relation to the data in Table 2(a). It is seen that in each case there are one or two large deviations which account for a substantial part of the chi square. This is, in part, a reflection of the general noisiness stack sampling data when measurements of parts per billion or parts per trillion are involved.

We have investigated the possibility that other independent variables may influence the outputs Y_i . Table 2(d) lists such potential variables. The most noteworthy data are the very large values of PCDF and PCDD in the input waste indicated by asterisks. The fact that these are for the PVC-free cases may be rather crucial to the failure of the previous analyses [13, 15] to see correlations between PVC and HCl and PCDF or PCDD.

One problem which makes it difficult to pin down the optimum functions of $Y_i(X, T, Z)$ is the relatively good correlation between temperature and carbon monoxide in the Vicon data. This may be expressed in the form

$$W = 10 \exp(a - bt) \quad (5)$$

where $a = 17.2$ and $b = 8.2$. Figure 1 illustrates this correlation which makes it difficult to determine whether a variation in Y_i is due to variations of T or CO.

Equation (3) lends itself to a reasonable physical interpretation which is consistent with many incinera-

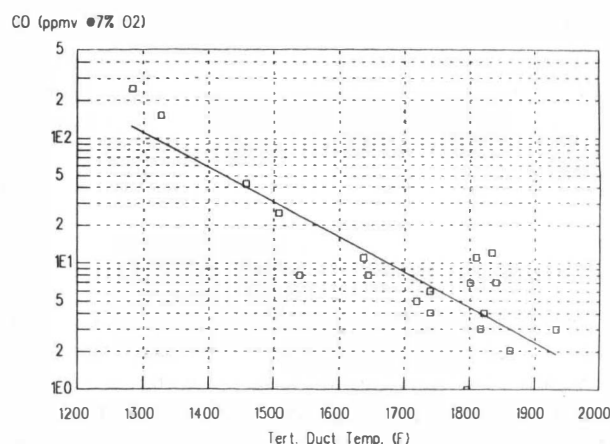


FIG. 1 CO AND TEMPERATURE AT TERTIARY DUCT

tor measurements in California [27], Canada [28], Denmark [29], Britain [30] and other areas. In effect, the second term becomes small when the incinerator is operated near optimum conditions. the first term may then represent the intrinsic limiting performance of the unit as it relates to the chlorine in the input or HCl in the output of the incinerator.

We have attempted to fit the Vicon-data set at the boiler exit by the same phenomenological models as given above. However, it is now generally recognized that additional dioxins and furans are created during the cooling process in the boiler. Accordingly, a more complicated set of dependent variables besides duct temperature, hydrogen chloride and carbon monoxide should be needed to phenomenologically characterize

chlorinated organic emissions at the boiler exit. However, when exiting a primary combustion chamber operating under good combustion conditions, one would expect all complex organic compounds to be destroyed, leaving only simple inorganic gases. Under these circumstances, we would expect the formation of complex organics during cooling in the boiler to be minimal particularly if there are no unchlorinated organic precursors such as benzene, phenol, furans or dioxins to undergo hydrogen to chlorine substitution. With these reasonable assumptions, our analytic modeling of chlorinated organics at the duct before entering the boiler should be directly relevant to an overall combustion control system for toxic minimization by the complete combustion system.

One potential weakness in the empirical equation phenomenological approach is the possibility that the equations chosen for testing might reflect one's prejudices. In an effort to insure against this possibility, we have also used linear multivariate statistical analysis on both the tertiary duct and boiler exit data to test the dependence of Y s upon temperature, carbon monoxide and HCl and the variables listed in Table 2(d). In effect, we have examined many relationships of the form

$$Y = a_0 + a_1t + a_2t^2 + a_3Z + a_4X' \dots + a_5h \quad (6)$$

$$+ a_6Cl + a_7O_2 + a_8f + a_9d$$

where h , Cl , O_2 , f , and d denote H_2O , Cl , O_2 furans and dioxins in the inputs. While in several cases our analyses showed sensitivities to the terms in the second row, unfortunately the availability of only 15 data sets at the tertiary duct and 19 at the boiler exit limits the possibility of fixing additional parameters. Concentrating on the variables t , Z and X , we obtained poor correlation coefficient when we assumed $Y_i(t)$. These improved dramatically when we assumed $Y_i(t, t^2)$. Adding $Z = CO/100$ as a variable generally improved these correlation coefficients as does adding HCl. In comparing $Y_i(t, t^2, Z, X)$, in all cases but one (P at duct) we obtained positive linear coefficients of X indicating that increased HCl correlates with increases in chlorinated organic emissions. These parameters are determined fairly sharply as indicated by the (error a_4)/ a_4 in several cases. The upper half of Table 3 gives the successive correlation coefficients and the lower half the coefficients for Eq. (6) assuming that the coefficients a_5 to a_9 vanish. The corresponding five parameter equations provide reasonable smooth characterizations of the tertiary duct and boiler exit emission data. As measured by the chi squares from the data [Table 2(a)] they do not do as well as Eq. (3) with the parameters in

Table 2(b). Nevertheless, either Eq. (3) or Eq. (6) can serve as a compact summary of the results of the Pittsfield-Vicon tests.

The Danish National Environmental Research Institute has conducted an extensive series of dioxin emission measurements on municipal and hospital incinerators. Measurements were carried out according to a statistical design following a plan of prerandomizer sampling. This procedure allowed causal interpretation of the correlations found between the dioxin emissions and certain operating parameters. They propose

$$\ln Y = a_0 + a_1RLD + a_2O_2 + a_3\ln HCl \quad (7)$$

where Y is the expected total sum of tetra- to octachlorinated dioxins and furans per NM^3 at 10% oxygen, a_0 is a constant for each incinerator, RLD is the relative load deviation from the design load; and O_2 is the deviation of oxygen content from 11% in the dry flue gas and $a_1 = 2.53$, $a_2 = 0.23$ and $a_3 = 0.19$. This equation may be rewritten in the form

$$Y = \alpha^2(HCl)^{a_3} \exp(a_1RLD + a_2O_2) \quad (8)$$

where $\alpha^2 = \exp a_0$. The exponential dependencies of Y on RLD and O_2 gives a large sensitivity to deviations from the design load or optimum combustion conditions. In this regard, Eq. (8) is physically similar to Eq. (3) and Eq. (6) in which combustion conditions are expressed explicitly in terms of the combustion variables, absolute temperature and carbon monoxide.

KINETIC MODEL OF CHLORINATED HYDROCARBON EMISSIONS

Prior Models

A number of theoretical approaches have been proposed to explain PCDD/PCDF formation processes in incinerators. Broadly speaking, these include: (a) the PCDD/PCDF output represents the unburned PCDD/PCDF in the input feed; (b) chlorophenols combine in the incinerator to form PCDD/PCDFs; (c) a variety of completely combusted organic compounds form unchlorinated dioxins or furans; then chlorine donors displace one, two, three, etc. hydrogen atoms to form PCDD/PCDFs; (d) fly ash catalyzes the combination of unchlorinated dioxins and furans with chlorine from chlorine donors; (e) reactions between Cl_2 and phenols form PCDDs and PCDFs. HCl participates indirectly by releasing Cl_2 via the Deacon reaction,

TABLE 3 CORRELATION COEFFICIENTS AND LINEAR MULTIVARIATE PARAMETERS
($Y = a_0 + a_1t + a_2t^2 + a_3Z + a_4X$)

	Tertiary Duct				Boiler			
	R ² (F)	R ² (D)	R ² (B)	R ² (P)	R ² (F)	R ² (D)	R ² (B)	R ² (P)
Y(t)	0.116	0.286	0.045	0.036	0.260	0.236	0.301	0.111
Y(t, t ²)	0.662	0.698	0.115	0.066	0.873	0.782	0.801	0.327
Y(t, t ² , Z)	0.706	0.732	0.230	0.154	0.905	0.854	0.805	0.330
Y(t, t ² , Z, X)	0.712	0.765	0.297	0.168	0.936	0.855	0.912	0.586
a ₀ =	1956	-440.8	-172.4	421.5	17816	5002	356.3	115.6
a ₁ =	-2704	481.1	203.7	-467.0	-22065	-6310	-422.3	-123.1
a ₂ =	938.6	-123.6	-59.26	131.7	6788	1999	124.8	33.81
a ₃ =	2.303	0.961	0.059	-0.137	9.128	3.797	0.116	0.046
a ₄ =	5.819	4.951	0.261	-0.369	32.67	1.258	1.171	1.290
Error a ₄ /a ₄	2.252	0.846	1.019	-2.476	0.386	5.260	0.241	0.339



Shaub and Tsang [32] and Penner, Weisenhahn and Li [33] have proposed detailed kinetic models of PCDD and PCDF production which focus on detailed congener production. It is thus difficult to correlate their results with the overall chlorinated hydrocarbon yields expressed as total PCDF, PCDD, chlorobenzene (ClBz) or chlorophenols (ClPh). The formation of PCDF and PCDD on fly ash has been proposed by Vogg et al. [18]. Christmann et al. [19] have found that during combustion and pyrolysis of pure polyvinylchloride (PVC) and PVC-cable sheathings in air, PCDD/PCDF are formed in significant amounts up to the ppm range. Thiesen et al. [20] have shown by studies of real fires and laboratory combustion tests that PVC-containing materials are PCDF/PCDD precursors.

More recently, Gullett et al. [21] have examined the formation mechanisms of chlorinated organics in a laboratory reactor. They find that PCDDs and PCDFs are mainly formed by reactions between Cl₂ and phenol at rates which depend upon temperature. They suggest that HCl participates indirectly via the Deacon reaction [Eq. (9)]. This reaction is enhanced by the presence of metal chloride catalyst in the ash, most notably CuCl₂. Thus, even though Cl₂ plays the direct role in the chlorination of organic precursors of the dioxins, an indirect cause and effect relationship between HCl levels and dioxins is indicated to an extent which depends upon temperature.

Most recently Tsang has shown that most of the binary reaction rates in a 36 × 36 matrix of possible light weight hydrogen, carbon and oxygen molecules

reactions in a flame are already known. Furthermore many reaction rates involving chlorinated hydrocarbon molecules are known. The large array of reaction which must be considered (~500 to 1000) suggest that it will be sometime before a kinetic approach which considers fluid dynamics and radiation is achieved. Accordingly, it is purposeful to attempt to find a simple kinetic approach which might serve a useful purpose in helping to understand combustion in an incinerator.

Kinetic Approach, Temperature Versus Time

The kinetic approach we are using incorporates a realistic temperature time history and a kinetics program developed in our earlier work on cofiring coal water slurries with natural gas [35-37]. In modeling the pyrolyses and combustion of coal, we used a temperature-time equation of the form

$$T = T_0 \exp(t/t_1) - (t/t_2) / [\Gamma + \exp(t/t_1)] \quad (10)$$

A realistic simulation of the 1800°F tertiary duct cases for the Pittsfield-Vicon experiments if $T_0 = 2034$, $t_1 = 0.4639$, $t_2 = 47.34$, (in sec) and $\Gamma = 1.035$. Fig. 2 shows this relationship.

Garbage Molecules

The pyrolysis code was originally developed for a macromolecular model of coal with a unit molecule such as C₃₅H₂₆O₃A which is compatible with coal mass fractions of carbon, hydrogen, oxygen and ash. The oxygen in the unit molecule was contained in loosely

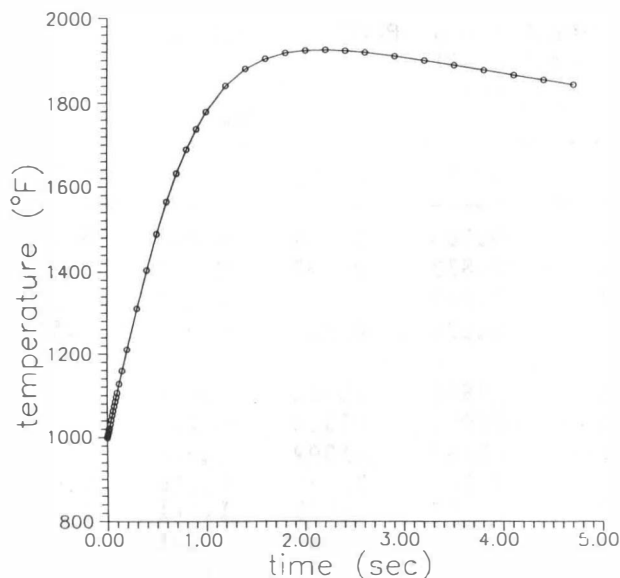


FIG. 2 TEMPERATURE VERSUS TIME

bound CO_2 and H_2O molecules which were released in the first pyrolysis step. Using institutional waste at Tacachale as a model we assume we have 25% by weight water, and 5% by weight ash, with the bulk mainly made up of plastics, paper, and some food stuffs. The plastics are comprised mostly of polystyrene and polyethylene with approximately equal fractions of the monomers $\text{C}_2\text{H}_3\text{C}_6\text{H}_5$ and C_2H_4 . The paper and food stuffs can be represented by the same fraction of the "monomer" $\text{C}_6\text{H}_{12}\text{O}_6$. To be comparable to the molecular weights of unit molecules used with the code previously, two of each monomer and an ash "atom" of atomic weight 48 were used for a unit molecule, $\text{C}_{32}\text{H}_{48}\text{O}_{12}\text{A}$, which has a molecular weight of 672. An additional 12 H_2O molecules accounts for 25% by weight water, but are not considered part of the unit molecule. The oxygen will again be contained in the loosely bound CO_2 and H_2O molecules, with an equal amount of each. The molecular formula can now be written as $\text{C}_{28}\text{H}_{40}\text{A} \cdot 4\text{CO}_2 \cdot 4\text{H}_2\text{O}$.

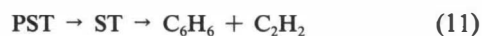
The kinetics code as used previously [35-37] looked only at C_1 hydrocarbon reactions. To better model the combustion of garbage, particularly plastics, additional reaction mechanisms have been considered. These should be global or semi-global reactions involving the conversion of polymer hydrocarbons to both simpler and more complex compounds in one or two steps, and then to chlorinated compounds in additional steps. Our original intent was to compare our kinetic model calculations to CCTL VOST data which typically includes chlorinated C_1 to C_3 hydrocarbons and chlorinated and

TABLE 4 INPUT CONCENTRATIONS TO THE KINETICS CODE FOR THE VICON DATA

Compound	Concentration kmol/m^3
O_2	2.040×10^{-3}
N_2	7.673×10^{-3}
garb = $\text{C}_{32}\text{H}_{48}\text{O}_{12}$	4.383×10^{-5}
H_2O (liquid)	5.702×10^{-4}
PST = polystyrene = $\text{C}_2\text{H}_3\text{C}_6\text{H}_5$	4.291×10^{-5}
PVC = polyvinyl chloride = $\text{C}_2\text{H}_3\text{Cl}$	7.140×10^{-6}

nonchlorinated single ring aromatics. However in view of the much greater investment made in the acquisition of the Vicon data and our own phenomenological modeling of this data we are using this unique data collection for our initial kinetic modeling studies.

Table 4 lists the initial inputs used for a representative Vicon trial burn. Figure 2 gives the temperature-time history we have chosen from the injection point to the tertiary duct. In our first go-around we did not include chlorinated organics, and we identified 32 compounds of hydrogen, carbon and oxygen which participate in various reactions. Using reaction rates, we have found in the literature we calculate the concentration of these species at 4.7 sec, the time a slug of the gases released at $t = 0$ will reach the tertiary duct. Next we assume that benzene (B_0) is generated from polystyrene via the reaction



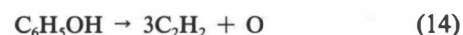
We generate phenol (P_0) by the reaction



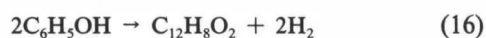
As an additional destruction path for benzene we use



and for phenol we use



We next assume that unchlorinated furans (F_0) and dioxins (D_0) are produced via



The upper section of Table 5 gives estimated inputs for Eqs. (11) to (16).

Next we consider the role of chlorine and pursue the tentative hypothesis that chlorinated organics are trace constituents formed by the chlorination of hydrocarbon products of incomplete combustion. Since, to our knowledge, none of these reaction rates are reported in the literature, again we estimate reasonable rates with the understanding that a single chlorination step mocks up the entire series of chlorinated organic congeners. Thus following the notation of the section on Phenomenological Models of Chlorinated Hydrocarbon Emissions we let $B_o(= Y_{30})$ denote C_6H_6 , $B(ClBz = Y_3)$ denote the total chlorobenzenes, $P_o(= Y_{40})$ denote C_6H_5OH and P denote total chlorophenols ($ClPh = Y_4$), $F_o(= Y_{10})$ denote $C_{12}H_8O$ and F denotes total chlorofurans ($PCDF = Y_1$) and $D_o(= Y_{20})$ denote $C_{12}H_8O_2$ and D denote total chlorodioxins ($PCDD = Y_2$). We next assume for each of these cases that chlorination proceeds via the exothermic reactions



The next section of Table 5 gives reaction rates which lead to results in reasonable accord with our phenomenological representations of the Vicon data. Figures 3(a-d) illustrates time dependent sets of concentrations which reflects such a calculational path. We have also investigated the possibility that HCl directly chlorinates the aromatics via the endothermic reactions



The lower part of Table 5 gives estimated RR. The results are quite similar to those shown in Figs. 3(a-d) except that no Cl_2 is generated.

SOCIO-TECHNICAL COMPONENT

Beginning in December 1987, the Clean Combustion Technology Laboratory has accumulated experience in co-combustion in a modular incinerator of nonhazardous waste (NHW) with natural gas (NG), much of the time with cellulosic biomass (CB). For the last 2 years, our focus has been on measuring toxic products of combustion and minimizing these products by precombustion and combustion measures.

The possibility of strong control of the input waste stream is the major feature which differentiates institutional solid waste management from municipal waste management and hazardous waste management, which have received almost all of the attention of federal pro-

grams. With guidance of the chief executive officer (CEO), an institution's purchasing agent can restrict the input into the institution's waste stream so as to minimize toxic materials (TM) and toxic producing materials (TPM). An institution can also develop source separation methods and motivational techniques to limit the TM and TPM entering its burn bags. In particular, restricting halogenated organic compounds and toxic metals in the input to the institution and further following a protocol of restricting their entry into the burn bags will substantially lower the production of corrosive and toxic products upon combustion. The use of transparent burn bags so that the combustor operator can finally visually inspect for TM or TPM adds a further protective measure to insure that the burn bags only contained NHW. In effect, the refuse derived fuel (RDF) produced by an institution can be subjected to four types of protective measures: (a) by the CEO; (b) by the purchasing agent; (c) by the home supervisor; and (d) by the incinerator operator.

During the course of pilot scale studies which began in December 1987, we have used several feedback systems in an effort to motivate each home to produce burn bags free of TM or TPM, difficult to burn materials, or cans, bottles and other recyclable materials. Prior to involving cottages in this program, a meeting was held with all the key staff in Facility 1 (120 beds, 260 employees, eight homes, 14-18 beds each). The project was explained, the expected outcomes identified, and proposed source separation and bagging procedures were discussed. Previously, all eight of the homes had used "community" 6- or 8-cu yd dumpsters for daily trash disposal. There were no existing rules or procedures for any type of TM or TPM separation system or internal recycling of any kind apart from on-site restrictions prohibiting glass containers in the homes. With the installation by the CCTL of 3-cu yd dumpsters at each cooperating cottage, a training program was instituted which could be summarized as follows: (a) each site supervisor met with all of the cottage staff, as well as the housekeeping staff, who actually were the most responsible for the actual bagging and dumping of the recyclables as well as the NHW burned at the CCTL incinerator; (b) responsibility for monitoring what actually ends up in the burn bag container at each home was assigned; and (c) each home manager met weekly to review progress, discuss and share ideas to improve source separation, bag tying, and wetness reduction and to discuss grades assigned in previous collections.

For the most part, these training procedures were quite effective, and in successive runs the amount of recyclables and toxic and hazardous components in the

TABLE 5 KINETIC MODEL REACTIONS AND THEIR RATES

For both models:

Reaction	Arrhenius rate factors $(\text{m}^3/\text{kmol})^{0.1,2}/\text{s}$	n	E/R K
garb \rightarrow tar + 4 H ₂ O + 4 CO ₂	1.83E-21	7.0	0.0
tar \rightarrow char + 20 CH ₂	9.14E-22	7.0	0.0
char \rightarrow 4 C ₂	4.57E-22	7.0	0.0
PVC \rightarrow HCl + C ₂ H ₂	1.72E+02	0.0	2320.0
PST \rightarrow ST	2.19E+02	0.0	1985.0
ST \rightarrow B ₀ + C ₂ H ₂	1.00E+11	0.0	5000.0
B ₀ + OH \rightarrow P ₀ + H	4.00E+08	0.0	5335.0
B ₀ \rightarrow 3 C ₂ H ₂	9.00E+06	0.0	19124.0
P ₀ \rightarrow 3 C ₂ H ₂ + O	2.00E+11	0.0	33216.0
P ₀ + P ₀ \rightarrow F ₀ + H ₂ O + H ₂	1.80E+02	0.0	5000.0
P ₀ + P ₀ \rightarrow D ₀ + 2 H ₂	7.00E+01	0.0	5000.0

For chlorination by Cl₂ via the Deacon reaction:

2 HCl + O \rightarrow Cl ₂ + H ₂ O	1.20E+11	0.0	0.0
B ₀ + Cl ₂ \rightarrow B + HCl	1.00E+01	0.0	5000.0
P ₀ + Cl ₂ \rightarrow P + HCl	2.50E+04	0.0	5000.0
F ₀ + Cl ₂ \rightarrow F + HCl	5.00E+06	0.0	5000.0
D ₀ + Cl ₂ \rightarrow D + HCl	5.00E+06	0.0	5000.0

For direct chlorination by HCl:

B ₀ + HCl \rightarrow B + H ₂	1.00E-01	0.0	5000.0
P ₀ + HCl \rightarrow P + H ₂	2.50E+02	0.0	5000.0
F ₀ + HCl \rightarrow F + H ₂	5.00E+04	0.0	5000.0
D ₀ + HCl \rightarrow D + H ₂	5.00E+04	0.0	5000.0

$$\text{reaction rate} = \text{RR} = A T^n e^{-E/RT} [\text{reactant}_1] \dots [\text{reactant}_n]$$
garbage = C₃₂H₄₈O₁₂A = C₂₈H₄₀.4H₂O.4CO₂tar = C₃₂H₄₈O₁₂ = C₂₈H₄₀.4H₂O.4CO₂char = C₈B₀ = benzene = C₆H₆P₀ = phenol = C₆H₅OHF₀ = dibenzofuran = C₁₂H₈OD₀ = dibenzodioxin = C₁₂H₈O₂ST = styrene = C₆H₅C₂H₃B = chlorobenzenes = C₆H_{6-i}Cl_iP = chlorophenols = C₆H_{5-i}OHCl_iF = chlorofurans = C₁₂H_{8-i}OCl_iD = chlorodioxins = C₁₂H_{8-i}O₂Cl_i

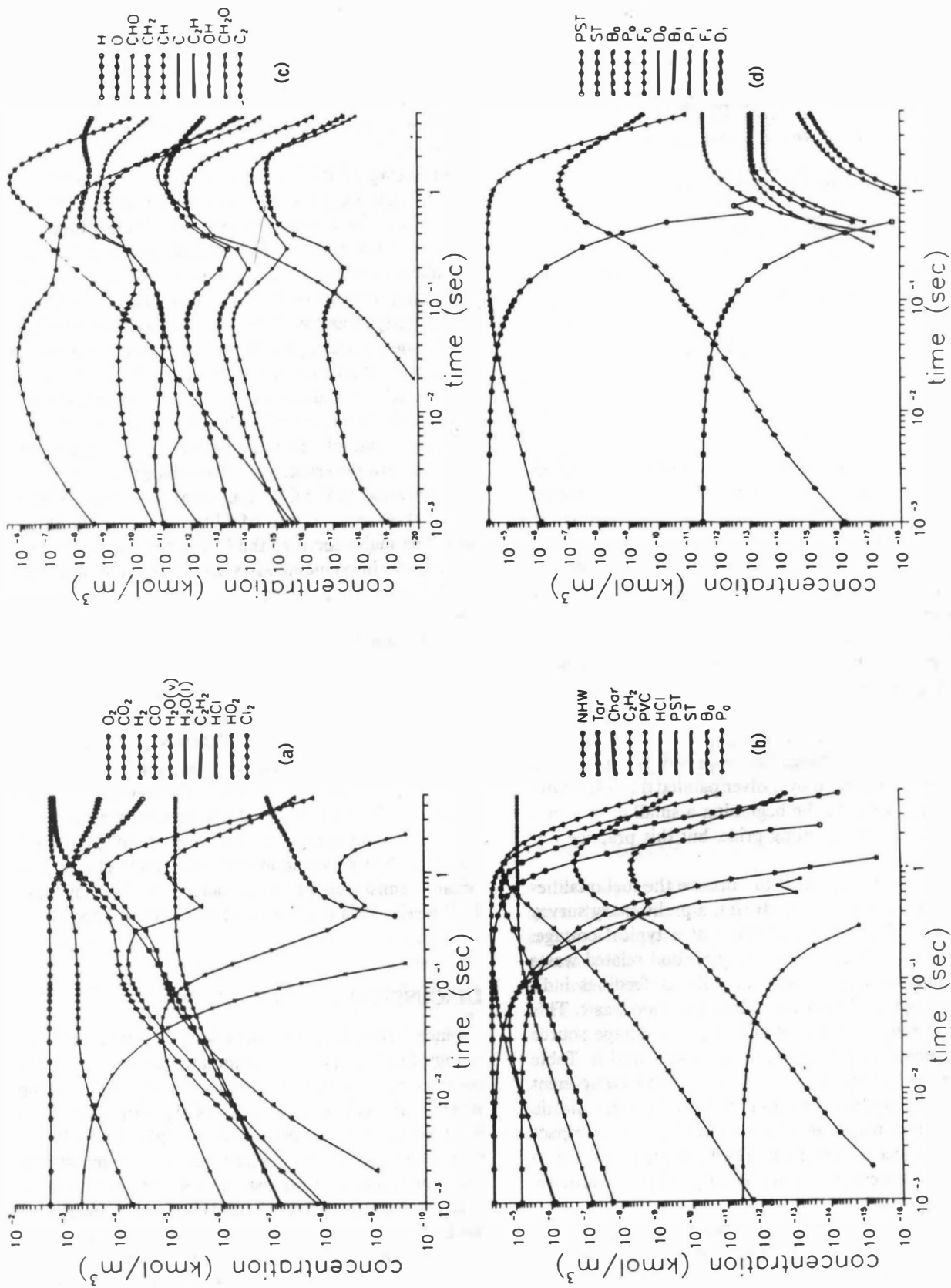


FIG. 3 CONCENTRATION VERSUS TIME: (a) MAJOR SPECIES; (b) FUELS; (c) MINOR SPECIES; AND (d) AROMATICS

TABLE 6 PROTOCOL FOR INSTITUTIONAL SOLID WASTE DISPOSAL

- (1) Food is to be shaken off liners and collected in one or two food trays and sent back to Food Service. Liquids are to be drained in sink.
- (2) Burnable food related waste and other burnable cottage waste are to be put in transparent bags and tied with identifiable strings or ties (for each facility within a unit).
- (3) Clean recyclables (cardboard, stacked paper, cans, bottles) are to be sent to Recycling.

Toxic or Hazardous material listed below are to be retained for Amnesty days.

Auto (automotive)	House (household)	Hobb (hobby products)	Haza (hazardous)
oils	cleaners	glues	aerosol cans
chemicals	polishers	cements	bottled gas
gasoline	deodorizers	inks	batteries (lead, watch flashlight)
fluids	solvents	paints	
	dyes	photographic materials	
	insecticides		
	degreasers		

CCTL dumpsters decreased. Occasionally, however, due to the greater convenience of dumping unwanted material in the CCTL dumpster at each cottage as compared to walking some 50–100 yards to the community dumpster, there was some backsliding. There appeared to be a need for a more positive feedback system or motivators to encourage recycling and source separation of TM or TPM, such as prizes, letters of appreciation, extra privileges, or monetary rewards. Thus, to encourage greater efforts towards source separation of the cottage waste we established a “Silver Dumpster Award.” Each week the cottage which scored highest in the quality of its bagged garbage had its regular 3-cu yd dumpster replaced by a silver painted dumpster with the project logo. In the beginning a small cash award accompanied this rotating prize, but this practice was not maintained.

In the intensified effort to improve the fuel qualities of the combustible waste stream, a preliminary survey was made of food related waste at a typical cottage. The results of a detailed sorting of food related waste following breakfast, lunch and dinner feedings indicated a high level of juices, drinks and food waste. This led to a reformulation of the rules of cottage source separation. The new protocol is summarized in Table 6. This protocol reduced the large food component previously experienced and increased the large plastic components which mostly consisted of high impact thermoformed polystyrene. The food reduction led to major improvements in the heating value of Tacachales’s waste.

The foregoing system was quite successful, and the CCTL expanded its trial burn program to twice a week by taking on Facility 2 consisting of nine cottages.

Unfortunately this effort was truncated by budget cuts which reduced our trial burn capabilities to one day per week. In an effort to maintain a competitive motivational system, we selected the four highest scoring homes from Facility 1 and the corresponding four from Facility 2 and resumed a one day per week burn schedule.

In Spring of 1990, a decision was made to go to a new overall Tacachale garbage collection system and to remove the garbage dumpsters. These dumpsters were not only eyesores, but they supported a large cat population and were sources of undesirable odors. Furthermore, over the course of a week many of the bags, particularly those torn by cats, collected rainwater. Under the new system, pick up trucks transferred from the University of Florida were used to collect and deliver Tacachale’s everyday cottage waste to a central compactor which periodically hauled to and unloaded at the county landfill. To maintain the CCTL experimental trial burn program, all of Tacachale’s cottage waste was delivered to the CCTL on trial burn days. After a while, these evolved into trial burns every other Saturday. The major focus of the CCTL tests since the new system was implemented has been on the measurement of HCl and chlorinated organic emissions. These results are noted in Table 1. It is clear that during this period we achieved low organic emissions when compared with typical California hospital incinerators, despite the fact that we were burning a higher level of plastics. Unfortunately, our HCl emissions have been higher since May 1990 by a factor of 3 or 4 at 150–200 ppm than they were during the previous year when we were working only with a select group of cottages. Nevertheless, we still achieved good effective scrubbing levels for organic compounds (of the order of 90%). Accordingly, we believe we should get still lower chlorinated organic emissions when we can get back to 50 ppm HCl levels. This is a thrust of our current efforts.

DISCUSSION

Since December, 1987 the Clean Combustion Technology Laboratory has accumulated experience in co-combustion in a modular incinerator of nonhazardous waste with natural gas, most of the time with high levels of paper products (~42%) and plastics (~39%). Our focus for the last 2 years has been on measuring toxic products of combustion and minimizing these products by pre-combustion and combustion measures. Such diverse and complex measurements with a full scale system, of course, do not lead to the measurement accuracy and variable control obtainable in laboratory

experiments. For example, our best original waste collection procedures before May 1990 gave HCl emissions lower than 1g/kg (1kg/t), whereas the new waste collection procedure yielded 2g/kg. Nevertheless, during the course of this effort we believe we have demonstrated an approach to clean waste combustion which should be applicable widely to hospitals, schools, prisons, military bases, and other institutions. The strong control of the input stream is a major feature which can insure the success of an institutional solid waste to energy system. With guidance of the chief executive officer (CEO), an institution's purchasing agent can restrict the input of the institution so as to minimize toxic materials (TM) and toxic producing materials (TPM). In addition to this pollution prevention measure, an institution can also develop source separation methods and motivational techniques to further limit the toxic material or toxic producing material entering its burn bags. By using transparent burn bags, the waste collector and the incinerator operator can visually inspect the bags and reject those with TPM, aerosol cans, batteries or recyclables.

Can measures which insure the clean combustible nature of institutional waste be applied to community waste? We believe so particularly by close knit, self reliant and environmentally conscious communities. While the CEO and purchasing agent would not have direct counterparts, a public education program could foster the same type of household responsibilities as assumed by Tacachale's households. If transparent burn bags are mandated, the garbage collector can quickly make a visual check for TPM, recyclables, etc. and simply leave bags which do not pass muster. The stigma of having unacceptable trash bags in front of one's home will provide a peer pressure for improved performance. The fact that the household itself must now dispose of the trash provides another incentive to avoid a reoccurrence of rejected bags.

This approach to improving the quality of community waste can be greatly facilitated if the federal or state government required clear labeling of toxic material or toxic producing material. Then a public education program could readily foster the same type of protective spirit as can be accomplished by precombustion measures at an institution. Accordingly, we believe much of what we have learned is applicable to community waste disposal.

Whether a program to decrease disposal chlorinated products will be efficacious in reducing HCl and chlorinated organic emissions has been widely debated. The conventional wisdom has been that this isn't worth the effort [13-15] and that post-combustion measures can handle anything. Our work indicates that in the case

TABLE 7 CLEAN COMBUSTION TECHNOLOGY FOR MEDICAL WASTE (Adapted from Green [5])

Pre-Combustion
<ol style="list-style-type: none"> 1. Send Cytotoxic, Hazardous and Radioactive chemicals to Toxic Depository. 2. Replace disposable Toxic Materials (TM) and Toxic Producing Materials (TPM), by non-TM and non-TPM. 3. Recycle reusables after sterilization. 4. Use motivational systems to insure sanctity of burn bags.
Combustion
<ol style="list-style-type: none"> 1. Coburn with natural gas as needed. 2. Use stoker, moving grates, auger, pulsed hearth or rotary kiln. 3. Afterburn (reburn) with natural gas. 4. Optimize temperatures and CO levels.
Post Combustion (as needed)
<ol style="list-style-type: none"> 1. Hot gas clean up. 2. Spray drier and fabric filter. 3. Venturi scrubber and packed tower. 4. Electrostatic precipitator 5. Immobilize or extract metals from ash. Monofill residues.

of chlorinated organic emissions this conventional wisdom is erroneous. Our thesis that input chlorinated organic material is manifested by output chlorinated organic emissions is supported by: (a) our HCl and VOC measurements; (b) our nonlinear empirical equation analysis of the Vicon data; (c) our linear multivariate analysis of the Vicon data; and (d) our kinetic modeling of chlorinated organic emissions from a Vicon type incinerator. In this last connection, we should note that our kinetic model is simplistic and based upon specific reactions. This modeling effort is now being extended to describe chlorination by steps in an effort to fit congenor data. The preliminary indications are promising. We have also examined several alternative organic chlorination models and have not yet found one which indicates that organic chlorine inputs have no influence on organic chlorine emissions.

CONCLUSIONS

Contrary to conventional wisdom, our work indicates that restricting chlorinated organic compounds and toxic metals in the input to an institution can very substantially lower the production of corrosive HCl and toxic volatile organic compounds in the stack emissions and also lower the toxic material in the ash [9, 10, 12]. Of equal or greater importance are improvements in combustion conditions in the primary and secondary stages. In our case, these were achieved early-on by added underfire and overfire air blowers and by incorporating a stoker to stir the burning waste. In effect, we abandoned the conventional starved air mode in favor of a stoichiometric or excess air mode in the primary chamber and also increased the temperature of the secondary chamber.

Table 7 and Fig. 4 illustrate precombustion, combustion, and postcombustion measures which should en-

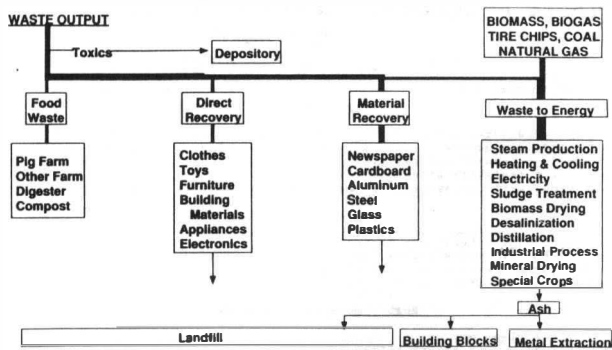


FIG. 4 COMPREHENSIVE WASTE MANAGEMENT SYSTEM FOR INSTITUTIONS AND SMALL COMMUNITIES

sure that an institution achieves an environmentally sound waste disposal system while maximizing its recycling yields. Key ingredients needed to insure success are the aggressive application of pollution prevention thinking and the maintenance of good combustion conditions.

ACKNOWLEDGMENTS

This work was supported, in part, by the University of Florida, the Florida Department of Environmental Regulation, the Tennessee Valley Authority and the Florida Energy Office, and a cooperative study with Tacachale (formerly Sunland of Gainesville). We thank Gene Hemp, Donald Price, Winfred Phillips, Robert Gaither, Philip Badger, Richard Strickland, and Barry Andrews for various forms of support which made this study possible. We are indebted to David English, Christopher Batich, Kenneth Wagener, Daniel Chang, Mike Bulley, Karen McNally, and Bruce Green who made important intuitive contributions during the formulation and evolution of this approach. We also thank Xie Qi Ma, Joseph Blake, David Powell, Jimmy Street, Charles Schmidt and Donald Clauson for their participation during the data gathering phases of this study. Finally we thank Scott Quarmany, Jonathon Carter, Tamara Markl, Christopher Jeselson, Jason Weaver, Michael Mahon and Scott Driskell for experimental and computational support.

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