Thermal Treatment of 1,2,3,4-Tetrachlorodibenzo-*p*-dioxin by Reaction with Ca-Based Sorbents at 23–300 °C

BRIAN K. GULLETT*

U.S. Environmental Protection Agency, Air Pollution Prevention and Control Division (MD-65), National Risk Management Research Laboratory, Research Triangle Park, North Carolina 27711

DAVID F. NATSCHKE AND KEVIN R. BRUCE

Acurex Environmental Corporation, P.O. Box 13109, Research Triangle Park, North Carolina 27709

The fate of combustion-generated polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) captured in sorbent-based, air pollution control devices remains uncertain. This process was simulated by passing vapor-phase 1,2,3,4-tetrachlorinated dibenzo-*p*-dioxin (TCDD) to a fixed-bed reactor laden with, typically, 1 g of calcium (Ca)-based sorbent. The sorbent bed, reactor rinsate, evaporation chamber, and gas impingers were analyzed separately to balance and account for the TCDD input. Tests at 160–300 °C demonstrated 50 to 100% conversion of TCDD to higher molecular weight, chlorinated products with both aromatic and aliphatic components. The unlikeliness of conventional semivolatile GC/MS analyses to detect these higher molecular weight products may offer an alternative explanation for research studies citing destruction or volatilization of chlorinated organics in the presence of Ca-based sorbents. The applicability of this reaction to other halogenated organics, such as polychlorinated biphenyls, may provide a method for contaminated soil treatment. More extensive experimental and analytical work is necessary to fully understand the reaction mechanism, the full range and stability of potential reaction products, and the ecological and human health implications. Alteration of the structural symmetry and size of the TCDD molecule (and related halogenated organics) will likely cause significant reductions in toxicity.

Introduction

Reaction or adsorption of chlorinated aromatics such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) with calcium (Ca)-based sorbents is of interest in the fields of air pollutant emission control and contaminated soil treatment. Spray dryer (SD) and fabric filter (FF) combinations have been employed to control air emissions of PCDDs and PCDFs from waste combustion sources (*1*), most notably municipal waste combustors (MWCs). Demonstrated field results with PCDD and PCDF sorption by Ca-based SD/FF combinations have led the U.S. Environmental Protection Agency (EPA) to use this technology as a control technology basis for MWC regulations (*2*). Recently, treatment experiments combining calcium oxide (CaO) sorbents and PCB-

contaminated soils (*3*, *4*), chlorinated hydrocarbons (*5*), and chlorinated benzenes (*6*) have explored the ability of Ca-based sorbents to react with and render harmless the chlorinated species. For both the emissions and soil applications, the mechanistic interaction of the chlorinated species with the sorbent is not well understood nor is the ultimate fate of any potential reaction products. Studies in this area are made difficult due to the extremely low concentrations of the reactants and potential products and the high analytical expenses involved.

Previous research studying the sorption of various gaseous chlorinated organic compounds on surfaces has found that these compounds can undergo what the authors term an "irreversible adsorption" or decomposition on the surface of MWC fly ash at temperatures above 100 °C (*7*). This adsorption was characterized by organic mass loss upon solvent extraction after exposure to elevated temperature and was not distinguished from decomposition or reaction to form other products. Specifically, 1,2,3,4-tetrachlorinated dibenzo-*p*-dioxin (TCDD) was shown to undergo increasing partial irreversible adsorption or decomposition on MWC fly ash between 100 and 300 °C in both air and helium atmospheres. Increased temperatures showed greater irreversible adsorption or decomposition to over 50% by mass above 250 °C (*7*). Similar findings were also extended to non-chlorinated dibenzo-*p*-dioxin and 1-monochlorodibenzo-*p*-dioxin with "loss" of reactant as high as 81 and 58%, respectively (*8*). Lower or higher chlorinated PCDDs were not detected, eliminating the possibility of conversion to related products.

A possible answer to the fate of chloroaromatics in CaO systems may have been reached by Dougherty and Collazo-Lopez (*9*) when they tested the gaseous emissions from the thermal destruction of polyvinylidene chloride in a 1000 °C tube furnace. The emissions were passed through a fluidized CaO bed resulting in a 300-fold decrease in aromatic polychloride effluents. It was speculated that CaO could react with carbon chlorine (CCl) molecular fragments at a temperature of 1000 °C to give calcium chloride (CaCl₂) and other products. Similar work by Ross and Lemay (*10*, *11*) found that PCBs could be destroyed in 500–800 °C systems when the chlorinated organics were passed through aluminum or aluminum oxides.

In research at lower temperatures, an EPA contractor (see Appendix A of ref 3) found that chlorinated organics such as PCBs underwent destructive reaction in the presence of CaO without added heat. Experiments indicated that reductions of PCB concentrations up to 90% were achieved in PCB/soil/CaO matrices; however, subsequent analyses by the EPA (*3*) showed that the losses of PCB reported were due to evaporation during exothermic CaO hydration and not due to a decomposition reaction. These results were independently supported by results (*12*) from similar experiments showing ≤6% loss of tetrachlorobiphenyl (TCB) during exposure to CaO.

Following these studies, Meta Environmental, Inc. (*13*) evaluated the effectiveness of CaO for treating PCB-contaminated soil and sand under several reaction conditions. Treatability experiments between about 80 and 250 °C showed a significant decrease (90%) in PCB levels in experiments above 200 °C that appeared primarily to be associated with thermal rather than chemical effects. However, the fate of the PCBs was not determined, and a mass balance on chlorinated products was not attained. Further research on quicklime/PCB interactions was not pursued (*14*).

Experiments by Koper et al. (*5*) have found destructive adsorption of nonaromatic chlorohydrocarbons (CCl₄, CHCl₃, C₂Cl₄) on high surface area (>100 m²/g) CaO at about 300–
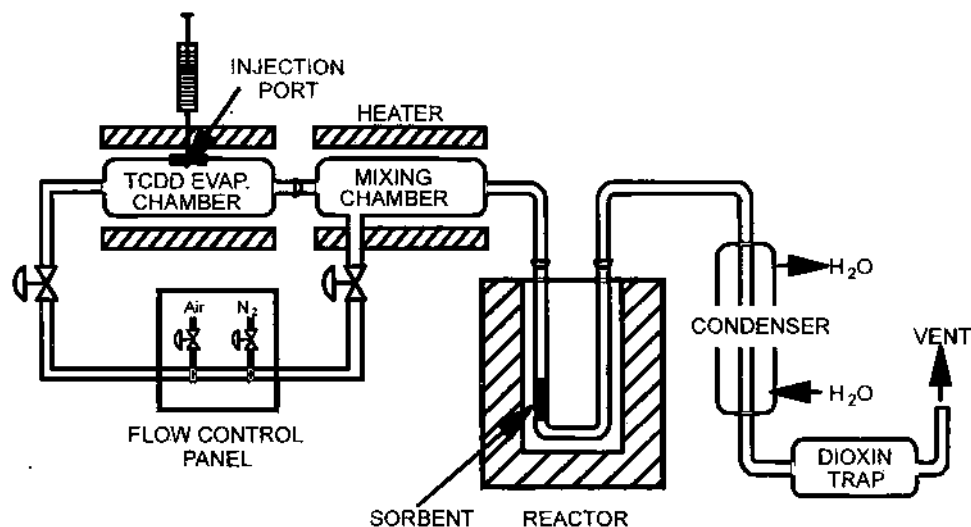
FIGURE 1. Schematic of the TCDD reaction apparatus.

400 °C. The main reaction products identifed included $CaCl_2$, CaClOH, CO_2, $CaCO_3$, and graphite. The work of Koper et al. was extended to the treatment of chlorinated benzenes by Li et al. (6). The latter found that the presence of CaO or MgO particles at 500−900 °C aided destruction over that of homogeneous thermolysis, forming partially chlorinated benzenes, benzene, phenol, CO, H_2O, and HCl. Runs with CaO and an air atmosphere at 900 °C also yielded traces of nonchlorinated dibenzo-p-dioxin and monochlorodibenzo-dioxin. This important evidence of heterogeneous reactive destruction at high temperatures raises additional questions regarding the fate of PCDDs/PCDFs in the lower temperature environment of emission control systems.

Many questions remain regarding the fate of chlorinated organics, such as TCDD, in low-temperature, Ca-based systems such as spray dryers or thermal soil remediation processes. Are the chlorinated organics destroyed by reaction with the Ca sorbent? Or are they simply volatilized? Or do the chlorinated organics undergo an irreversible binding to the surface such that recovery balances implicate a net loss of the compound? Answers to these questions are hampered by the considerable difficulties involved in detecting trace quantities of the decomposition or reaction products, allowing closure of a mass balance. In our research, we attempted to determine the fate of vapor-phase chlorinated aromatics in sorbent systems by passing TCDD through a fixed sorbent bed system followed by a rigorous TCDD and product balance.

Experimental Section

Reactor Tests. The reactor apparatus (Figure 1) consists of an evaporation chamber, a heated mixing chamber, a sorbent reactor furnace, and sampling apparatus (condensation and dioxin trap). Known quantities of 1,2,3,4-tetrachlorinated dibenzo-p-dioxin (TCDD) in toluene ($C_6H_5CH_3$) were injected through a rubber septum into a quartz evaporation chamber heated to above 330 °C. Baseline TCDD injection amounts were 100 ng (per 10 μL toluene) but for other experiments varied between 100 and 10 000 ng. The vaporized injectant was swept by the process gases through heat-traced glass tubing to the reactor, which was held at the desired experimental temperature (32−350 °C). The carrier process gas throughout most of the experiments was N_2, although some experiments included 10% oxygen (O_2) as well.

The reactor furnace consisted of quartz tubing containing a fixed bed of 1−3 g of sorbent suspended on fritted quartz and quartz wool. Typical process gas flow rates were 180 mL/min (standard temperature and pressure, STP), resulting in a gas/sorbent contact time in the reactor between 50 and 450 ms. A number of tests at elevated flow rates (383 mL/min, STP) ensured that there were no transfer limitations.

After exiting the reactor zone, process gases passed through, typically, three toluene-filled impingers designed to capture any vaporized TCDD and other organic reaction products. Typical experiments were 30 min from the time of TCDD injection to the time of reactor cooling. The sorbents tested were derived from a single commercial source, the Tenn Luttrell Company of Luttrell, TN. Commercial $Ca(OH)_2$ and $CaCO_3$ were used as well as CaO of increased surface area derived by thermally dehydrating $Ca(OH)_2$. The median particle size for the $Ca(OH)_2$ and CaO was 2.2 μm while the $CaCO_3$ was 10.1 μm. The specific surface area of the $Ca(OH)_2$ was 22.8 m²/g, the CaO was as reported, and the $CaCO_3$ was 1.2 m²/g.

The reactor exit gases were collected and/or analyzed with several systems over the course of this work. Potential reaction products were collected with three substrate systems: toluene-filled impingers, Amberlite XAD-2 sorbent resin cartridges, and Tenax sorbent resin tubes.

Product Detection. The exit gases from most of the reactor runs were collected by three toluene-filled impingers configured serially. These impingers were chilled in an ice water bath to reduce toluene evaporation and to enhance the capture of any organics passing through the system.

At the conclusion of each experiment, the reactor system was cooled, and component parts were analyzed for TCDD. The reactor was prepared as three samples: sorbent, post-sorbent tubing, and pre-sorbent tubing. The pre-sorbent tubing, including the evaporation chamber, was rinsed with toluene, concentrated, and analyzed by GC/MS for TCDD. Solvent rinses of the evaporator following nonsorbent control tests and subsequent experimental tests typically showed that little detectable TCDD remained in the evaporation chamber or the connecting tubing. The sorbent bed and post-sorbent tubing rinsate from the reactor zone were extracted with toluene and analyzed for TCDD by a method described previously (15).

The sorbent and rinsate samples were analyzed by GC/MS using the isotope dilution technique. Isotopically labeled homologues of 1,2,3,4-TCDD were used to quantify the native 1,2,3,4-TCDD present in the reactor samples and to assess method recovery. Prior to overnight toluene soxhlet extraction, the samples were spiked with a known concentration of [$^{13}C_{12}$]1,2,3,4-TCDD. Following extraction, the samples were concentrated and subjected to a series of chromatographic cleanup columns (acid/base silica, alumina, and activated carbon) to remove analytical interferants. The samples were then concentrated to a known value and spiked with the [$^{13}C_6$]1,2,3,4-TCDD recovery standard and analyzed by GC/MS.

In several experiments, more rigorous sorbent extraction was carried out to ensure that TCDD did not become irreversibly bound to the sorbent, thereby preventing detection with the normal toluene extraction. After spiking the sample with labeled standards, the reacted sorbent was dissolved in dilute HCl (1 N). The aqueous solution was then extracted with dichloromethane in a separatory funnel to remove organics, and the dichloromethane extract was concentrated and analyzed by GC/MS.

The GC/MS system is calibrated by determining the response of a fixed mass of $[^{13}C_{12}]1,2,3,4$-TCDD relative to the response of the varied mass of unlabeled 1,2,3,4-TCDD. The resulting relative response factors are then used to quantify the unlabeled TCDD present in each sample based on the known mass of $[^{13}C_{12}]1,2,3,4$-TCDD present in each sample. Similarly, response factors developed between the $[^{13}C_{12}]$-1,2,3,4-TCDD internal standard and the $[^{13}C_6]1,2,3,4$-TCDD recovery standard are used to quantify the method performance by determining $[^{13}C_{12}]1,2,3,4$-TCDD recovery.

Attempts were made to detect possible organic reaction products other than TCDD. Separate volatile and semivolatile organic samples were collected using organic adsorbent media specific to the boiling point ranges of potential organic reaction products (16, 17). Tenax GC was used to collect volatile compounds (boiling points between 30 and 140 °C), and Amberlite XAD-2 was used to collect semivolatile compounds (boiling points between 120 and 300 °C). Potential volatile and semivolatile reaction products were analyzed by thermal desorption followed by cryogenic focusing and injection onto a GC/MS. Tenax is a polymeric resin used for the capture of volatile organics in air sampling. Prior to use, the resin was cleaned by thermal desorption under flowing nitrogen. Desorption was accomplished by heating the sample to 300 °C. Desorbed components were swept from the cartridge to the GC inlet with flowing helium. Prior to use, the Amberlite XAD-2 resin was cleaned by solvent extraction and dried under flowing nitrogen. After sampling, the resin was transferred from the sampling cartridge to the thimble of a Soxhlet extractor. The sample was extracted overnight with methylene chloride. The extract was then transferred to a Kuderna–Danish concentrator and concentrated prior to analysis by EPA Method 8270 (18). Tests with both resins were conducted using high levels of labeled and unlabeled TCDD (5000 and 8500 ng, respectively) in order to enhance detection of possible reaction products.

In an effort to identify CO and/or CO_2 as possible inorganic gaseous reaction products, an Ametek Dycor M200MBCDF residual gas analyzer (RGA), a low-resolution mass spectrometer, was connected to the reactor exit gases and used to provide real-time analysis for potential reaction products. The RGA pulled a side stream, less than 1% of the total gas flow, prior to the toluene impingers. An XAD-2-filled canister was placed upstream of the Dycor to remove possible organic interferents. Large loadings (8 000–10 000 ng) of $^{13}C_{12}$-labeled TCDD were injected into the evaporation chamber for these experiments. The RGA was set up to monitor the 41–46 atomic mass unit (amu) window in an attempt to identify CO_2 (44 amu) and $^{13}C_{12}$-labeled carbon dioxide (CO_2) (45 amu) as a reaction product by distinguishing between ambient (control) and test reactor exit gas concentrations of labeled CO_2. Process gas flow rates were decreased to approximately 15 mL/min to increase possible CO_2 concentrations.

Additional experiments were conducted to provide materials for a more rigorous product detection effort. In two runs (A and B), the evaporation chamber was held at 225 and 263 °C (versus nominally 330 °C) to avoid any possible thermolysis of the injected TCDD. TCDD (5000 ng) was injected into the evaporator chamber, and the run was continued for 1 h to promote complete evaporation of the TCDD from the evaporator. A 1-g sample of $Ca(OH)_2$ was used in the reactor for each run.

In order to analyze for nonvolatile reaction products, a gravimetric analysis of the reaction products was undertaken. Sorbent samples were generated with the Figure 1 reactor apparatus, and as before, the glassware, toluene impingers, and the sorbent sample were acid-neutralized, extracted with dichloromethane, concentrated, filtered, and then analyzed gravimetrically. A measured aliquot of an extract from the sorbent was transferred to a tared aluminum weighing pan, air-dried, and then desiccated overnight with silica gel. Thus, any possible volatile products would be released prior to desiccation and any semivolatile organics (compounds with boiling points <315 °C) should be removed by the silica gel desiccant.

After completion of the gravimetric analysis, the sample was recovered by rinsing with dichloromethane for further analysis. Complete sample recovery was ensured by repeating the process until (1) sample exposure to ultraviolet (UV, 254 nm) light showed no fluorescence from conjugated, multiple-bonded structures and (2) the pan had returned to its tare weight. The sample-containing solvent rinse was then concentrated under a flowing N_2 stream to less than 5 mL of remaining volume. The concentrated sample was transferred to a volumetric flask and made up to final volume (5 mL) with additional dichloromethane.

The recovered sample was subjected to thin layer chromatography (TLC) in order to separate the nonvolatile compounds recovered from the gravimetric analysis. A Kontes TLC plate streaker was used to apply the entire extract to the pre-adsorbent strip of a Whatman LK6F plate. After the solvent had evaporated, the plate was inserted into a development tank equilibrated with hexane. Upon removal from the tank, the solvent front was marked and the plate was air-dried. For comparison purposes, 1,2,3,4-TCDD was also chromatographed on a separate plate. Separated fractions were detected by UV light exposure in an Ultra-Violet Products, Inc. Model C-70 Chromato-Vue Cabinet. Both short (254 nm) and long (366 nm) UV wavelengths were used to detect organic material. Detected fractions were marked. Relative retention factors (RFs), measured from the sample origin on the TLC plate, were calculated for all detected fractions as the elution distance divided by the solvent front distance. Detected fractions and their associated silica gel were scraped from the glass plate with a cleaned razor blade. These scrapings were transferred to the barrel of a glass Luer-Loc syringe, which was fitted with a Supelco ISO-DISC-P-254 disposable PTFE membrane filter (0.45 μm). Organic material was extracted from the silica gel with dichloromethane and transferred to a volumetric flask. The silica gel was extracted thrice in this fashion. The sample extract was made up to volume (2 mL) with additional dichloromethane.

Transmission infrared spectra were obtained on a Nicolet Model 550 FTIR. Samples were prepared as potassium bromide (KBr) pellets by adding the extract to 200 mg of dried KBr. Solvent was removed by evaporation under flowing N_2 before forming the pellet. After obtaining a spectrum, the sample was recovered for further analysis by crushing the pellet and extracting with dichloromethane. Samples recovered from the KBr pellets were solvent exchanged to deuterated chloroform.

Results and Discussion

Reactor Tests. Nine control tests at varying temperatures were conducted without sorbent to measure the effectiveness of the system at delivering the TCDD sample through the reactor to toluene-filled impingers without loss of mass. Temperatures for these tests varied between 106 and 346 °C, and input TCDD was constant at 100 ng. The results are shown in Figure 2 as TCDD change versus reactor temperature, T, where the amount of change is unity less the summed fraction of TCDD found in analysis of the quartz wool plug, impingers, and reactor washings. The results show a linear regression of the data and the 95% confidence intervals,
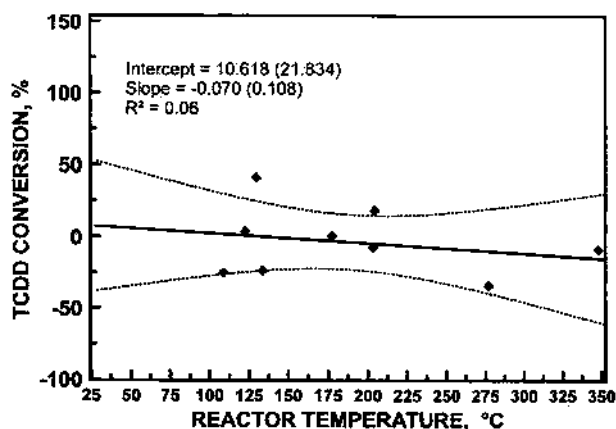
FIGURE 2. Effect of temperature on conversion of TCDD without sorbent (control experiment).
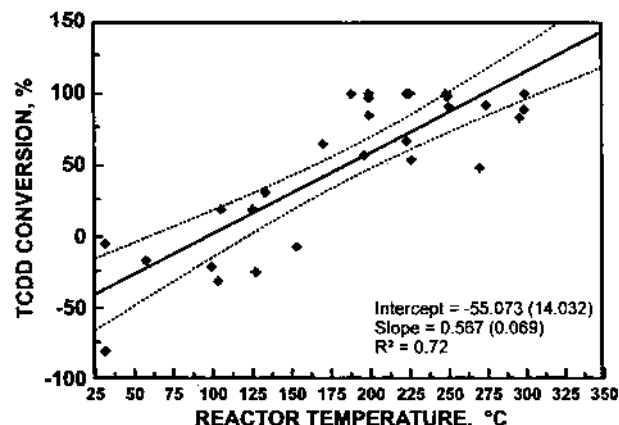

FIGURE 3. Effect of temperature on conversion of TCDD with Ca-(OH)₂.

indicating little or no loss of TCDD and passage of the injected TCDD through the system and into the impingers. This closed the mass balance for TCDD and indicated that any TCDD undergoing conversion or found in the reactor sorbent extract in subsequent tests is caused by interactions with the sorbent as opposed to purely thermal effects.

Direct doping of TCDD onto ambient temperature sorbent followed by nitric acid (HNO_3) extraction showed high (>90%) recoveries of the doped TCDD. No distinction was found between the two extraction techniques (Soxhlet extraction versus liquid–liquid extraction of acid-neutralizing sorbent), eliminating concerns of irreversible adsorption at ambient temperature.

Twenty-nine tests on the reactor were conducted under "baseline" conditions, varying only temperature (between 32 and 300 °C) and TCDD/sorbent "loading" (between 33 and 400 ng/g). A regression line of these 29 test results and the associated 95% confidence bands are shown in Figure 3. Here, TCDD conversion, X, is defined as

$$X = \frac{(TCDD_{IN} - TCDD_{OUT})}{TCDD_{IN}} \times 100 \qquad (1)$$

where $TCDD_{IN}$ is the mass of TCDD fed in ng and $TCDD_{OUT}$ is the summation of the TCDD mass found in analysis of the sorbent plug, impingers, and reactor washings.

Figure 3 clearly shows conversion of TCDD for temperatures in which the lower confidence band exceeds zero, i.e., ≈ 125 °C. Note that negative X values reflect limitations of accuracy and precision of the analytical methods and do not imply production of TCDD at these lower temperatures. Other parameters were varied outside of the range of the above 29 tests, and the subsequent results were tested for their
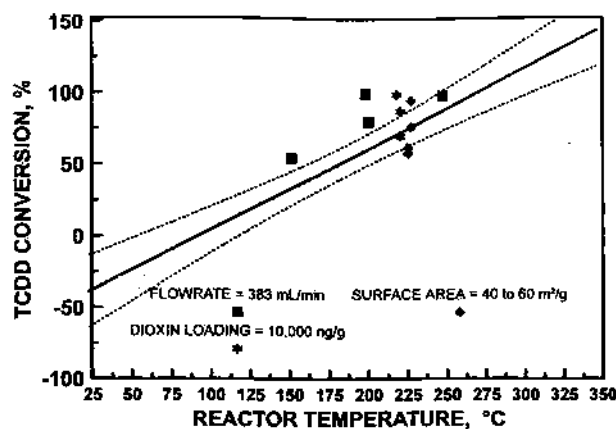

FIGURE 4. Effects of surface area, dioxin loading, and gas flow rate on conversion of TCDD as compared to Figure 3 baseline results.
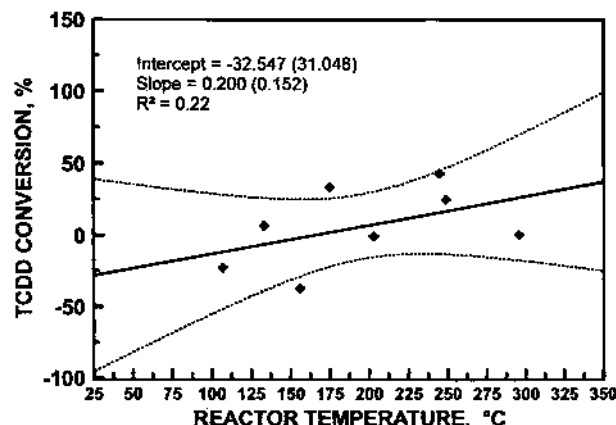

FIGURE 5. Effect of temperature on conversion of TCDD with CaCO₃.

significance in comparison to the $Ca(OH)_2$ results' regression. Figure 4 shows the effect of increased flow rate (383–388 mL/min versus 134–187 mL/min for the baseline), surface area (CaO: 40–60 m²/g versus 15 m²/g for the baseline Ca-$(OH)_2$), $TCDD_{IN}$ (10 000 ng versus 100–200 ng for the baseline), and loading (between 33 and 400 ng of TCDD/$g_{SORBENT}$) plotted against the regression and confidence limits of the baseline data (Figure 3). Statistical analysis showed only marginal statistical significance (compared to the 29 baseline tests) for higher flow rates and dioxin loadings ($TCDD_{IN}$) leading to higher values of X. No statistical significance (compared to the baseline tests) could be attributed to the effect of surface area. The lack of a surface area effect over a wide range (Ca(OH)₂ at 15 m²/g versus CaO at 40–60 m²/g) suggests that the sorptive or reactive capacity of the sorbent is not limited by surface phenomena.

Further proof of conversion with $Ca(OH)_2$ is gained by analysis of the subset of 18 data points with temperature above 175 °C. These points have an average X of 86.75% with 95 and 99% lower confidence bounds for the true mean conversion (T > 175 °C) of 79.55 and 76.15%, respectively. In other words, we can be 95% (99%) certain that the average X when T > 175 °C is no lower than 79.55% (76.15%).

Nine tests were conducted with CaCO₃ to measure its ability to convert TCDD. Temperatures between 107 and 296 °C and loadings of 100–400 ng TCDD/$g_{SORBENT}$ showed only slight evidence of non-zero and increasing conversion with temperature (Figure 5).

The reactivity differences observed between the three Ca-based sorbents may be due to particle size and basicity distinctions; the $Ca(OH)_2$ and CaO sorbents have 25 times the external surface area of the CaCO₃ and act as stronger bases for possible Cl abstraction.

A limited number of tests were conducted to assess the effect of O_2 in the process gas versus all N_2 on the fate of

TABLE 1. TCDD and Product Balance from Extended Method 8270

location	detected products 1,2,3,4-TCDD	RF = 1.004	RF = 1.021	RF = 1.024	total (mg)
impinger	0	0	0	0	0
glassware	1.0	0	0	0	1.0
sorbent	0.06	0.22	0.25	0.59	1.12
total (mg)	1.06	0.22	0.25	0.59	2.12

TCDD. Experiments were run with 10% O_2 in N_2 and a Ca-$(OH)_2$ sorbent. The sorbent and tubing rinse/impinger XAD were analyzed separately. The results in the presence of 10 vol % O_2 were not distinctive from the 29 baseline condition runs in N_2 only.

Product Detection. Efforts to verify the TCDD/Ca-based sorbent reaction focused on detection and then identification of the reaction products. Analytical efforts were focused on carbon and/or organic detection and organic mass balances rather than a chlorine balance. Our available instruments and methods were unlikely to detect inorganic chlorine products such as HCl, Cl_2, $CaCl_2$, or CaClOH due to detection limits of the available instruments and modest levels of chlorine present as an impurity in the sorbent. Efforts were therefore made to detect and identify possible trace CO, CO_2, chlorinated organic, and nonchlorinated organic products of the reaction.

Experiments with 8500 ng of [$^{13}C_{12}$]1,2,3,4-TCDD in nonane (C_9H_{20}) using the RGA to determine the potential for complete breakdown of TCDD by the sorbent to smaller molecules showed no detectable formation of labeled $^{13}CO_2$ (MW = 45 amu). Possible incomplete oxidation to labeled CO (^{13}CO, MW = 29) could not initially be confirmed or discounted because of masking by a prominent peak at 29 amu from a naturally present, isotopic form of the N_2 carrier gas ($^{14}N^{15}N$). Subsequent tests using helium (He, MW = 4 amu) as the carrier gas refuted the possibility of CO evolution from TCDD destruction within the detection limitations of the instrumentation.

Chlorinated aromatic or nonaromatic organic reaction products are relatively easy to identify through GC/MS methods because of the distinctive isotopic split between ^{35}Cl and ^{37}Cl. However, analyses of the Tenax and Amberlite substrate samples indicated that no volatile (approximated boiling point range = 25–100 °C) or semivolatile (approximate boiling point range = 100–300 °C) chlorinated products were found in concentrations significantly greater than the backgrounds for both sampling techniques.

An extended Method 8270 (18) analysis was performed on the extracted sorbent sample from one experiment in an effort to detect potential TCDD/Ca-based sorbent reaction products and to determine whether or not the products are of higher molecular weight (lower volatility) than that of TCDD. This analysis differs from the dioxin-specific protocol in that the column chromatographic cleanup steps designed to remove non-dioxin or non-furan products are not performed and the mass selective detector (MSD) is operated over the full responsive range of masses available on the instrument rather than scanning specific, dioxin- or furan-related masses intensively (selective ion monitoring or SIM mode). While reducing sensitivity of the instrument, this allows detection and possibly identification of a broader range of products. The analyzed sample was generated by introducing 5 mg of 1,2,3,4-TCDD into the 225 °C reactor containing 1 g of Ca-$(OH)_2$.

These analyses detected three non-TCDD reaction products in the sorbent (Table 1), which comprise 95% of the TCDD mass delivered to the sorbent bed (1.0 mg of TCDD condensed on the glassware prior to reaching the sorbent).
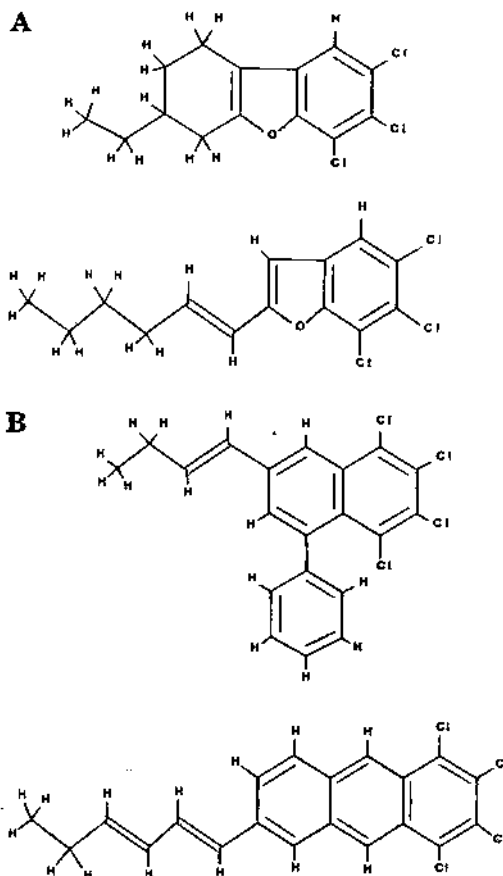
FIGURE 6. Potential structures for observed spectra. (A) Cluster with RF = 1.004, m/z = 302, empirical formula $C_{14}H_{13}OCl_3$, unsaturation index of 7. (B) Cluster with RF 1.021, m/z = 394, empirical formula $C_{20}H_{14}Cl_4$, unsaturation index of 12.

The remaining 5% of the mass consisted of unmodified TCDD. Normalizing the retention times of the three unknown compounds to the retention time for 1,2,3,4-TCDD yielded relative retention factors (RF) of 1.004, 1.021, and 1.024, suggesting that the three detected products have higher molecular weights than TCDD. A search of the mass spectrometry software library was unable to match known reference spectra with the three unknown compounds.

For the peak at RF = 1.004, the most significant feature of the spectrum is the cluster beginning at a mass/charge ratio (m/z) of 302. Isotopic abundance calculations on the 302 cluster are consistent with 3 chlorine, 14 carbon, and 1 oxygen atoms. The remainder of 13 is assigned to hydrogen atoms, yielding an empirical formula of $C_{14}H_{13}OCl_3$ and resulting in an unsaturation index of 7. The spectrum is consistent with losses of Cl and CO and results in a spectrum similar to 1,2,3,4-TCDD. Additionally, there is a loss of 36, which is consistent with a loss of HCl. Figure 6A shows two structures that could result in the observed spectra.

The peak at RF = 1.021 has a main cluster at m/z = 394 with the largest group of peaks beginning at 379. Isotopic abundance calculations on the main cluster are consistent with 20 carbon and 4 chlorine atoms, with the remaining 14 assigned to hydrogen atoms, yielding an empirical formula of $C_{20}H_{14}Cl_4$ and an unsaturation index of 12. The peak at 379 is assigned to a loss of CH_3 (15 amu) from the parent peak, while other peaks in the spectrum are consistent with losses of other alkyl groups and Cl. Figure 6B shows two possible structures that could result in the observed spectra.

The spectrum of the peak at RF = 1.024 is, in nearly every respect, identical to that for the peak at RF = 1.004. A major cluster is again found at m/z = 302, isotopic abundance calculations are consistent with 3 chlorines and 14 carbons,

TABLE 2. TCDD and Product Balance from Runs A, B, and C[a]

	run A	run B	run C
av. evaporation chamber temp	225 °C	263 °C	185 °C (permeation vial)
input $TCDD_{IN}$, mg	5.04	4.95	50.15

TCDD/Products Found, mg (% of input)

	gravimetric analysis			
location	run A	run B	run C	GC/MS TCDD analysis
inlet glassware	2.01 (39.9)	1.00 (20.2)	2.518	1.740
cold spot	NA	NA	37.396 (79.6)	34.130 (71.5)
sorbent	2.95 (58.5)	4.08 (82.4)	0.504 (1.0)	0.002 (0.0)
outlet glassware	NSA	NSA	5.783 (11.5)	5.570 (11.1)
impinger	0.27 (5.4)	ND	3.480 (6.9)	0.826 (1.6)
total	5.23 (103.8)	5.08 (102.6)	49.681 (99.1)	42.268 (84.3)

[a] ND, none detected. NA, not applicable. NSA, not separately analyzed; analyzed with impinger.

and the unsaturation index is 7. The breakdown patterns also match between these two spectra, indicating losses of Cl, CO, and HCl. Based on the higher retention time, it is likely that the molecular weight of this compound is significantly higher than 302, suggesting that no parent peak was found and making speculation about the potential structure impossible.

While identification of reaction products from the preceding test is tentative at best and represents only the gas chromatographable products, the previous tests detected TCDD/Ca-based sorbent reaction products and provided evidence that the products are not wholly inorganic gases, volatile or semivolatile organics, or low (<TCDD MW) molecular weight chlorinated organic compounds. Results suggested that a large fraction of the TCDD reactant becomes a compound of significantly larger molecular weight. However, since the analytical methods employed were not appropriate for providing definitive mass closure, repeat tests with different analytical methods were conducted.

To demonstrate mass balance of the input TCDD and to begin the search for higher molecular weight products, three additional reactor runs (A, B, and C) were completed for a GC/MS and gravimetric analysis. In these runs, the glassware, toluene impingers, and the sorbent sample were acid-neutralized, extracted with dichloromethane, concentrated, filtered, and analyzed. In run C, a TCDD-laden permeation vial swept with N_2 gas carried the TCDD to the sorbent bed. This N_2 carrier was used in place of the toluene carrier to ensure that the presence of toluene was not related to TCDD loss. The gravimetric results of these tests are found in Table 2. All three of these runs achieved an excellent mass balance with the input TCDD, indicating that all of the TCDD and reaction product(s) had been accounted for by our sampling methods and gravimetric analyses. A significant difference between these reactor runs is found in the mass distribution between the inlet glassware and the sorbent and beyond. It is likely that differences in the evaporation chamber temperature (runs A and B) and the experimental setup (run C) are responsible for varied percentages of delivered TCDD. TCDD was identified as the only compound observed in the inlet glassware, indicating that thermal decomposition was not occurring.

A comparison (Table 2) of run C mass values from GC/MS analysis, which only reports TCDD, and gravimetric analysis, which reports all product mass, provides insight to the fate of TCDD. The low amount of GC/MS-detected TCDD in the sorbent (0.002 mg) as compared to the larger amount from the gravimetric analysis (0.504 mg) indicates that very little of the sorbent-bound compounds are TCDD. The balance of the compounds represents reaction products derived from TCDD. The near-identical mass values from the outlet glassware suggest that all of the post-sorbent, condensible

TABLE 3. Retention Factors for Table 2 Products

fraction	run A RF	run B RF
1	0.019	0.015
2	0.425	0.188
3	0.954	0.375
4	1.000	0.598

material is TCDD. This is in sharp contrast to runs A and B where only minor amounts (if at all) of TCDD were found to pass through the sorbent bed. This may be due to significantly higher TCDD mass loadings on the sorbent in run C causing breakthrough. The GC/MS impinger results for run C confirm TCDD breakthrough, but the large mass difference in comparison with gravimetric results suggest that significant amounts of other reaction products reached the impinger solution. Because these non-TCDD products did not appear to condense on the outlet glassware, it suggests that their molecular weights are lighter than that of TCDD. This is not consistent with GC/MS findings from runs A and B (not shown) but is likely due to experimental differences. Runs A and B were 30-min tests at 225 °C with the Figure 1 apparatus whereas run C took over 30 h to feed the high amount of TCDD from the diffusion vial system into a 300 °C reactor. It is likely that, during the extended times at higher temperatures, some of the reaction products thermally decomposed to lower molecular weight compounds.

For product identification purposes, the sorbent samples from runs A and B were recovered from the gravimetric pans by rinsing with dichloromethane. These extracts were then separated by thin layer chromatography (TLC). For the extracts from both runs, four fractions were detected under ultraviolet light, indicating the presence of aromatic ring structures. Table 3 presents the relative retention factors (RFs) for these two experiments. The apparent differences in the RFs for the two experiments are due to the use of two different eluents. Reactor run A was eluted with 90 % hexane and 10% dichloromethane, while run B was eluted with 100% hexane. Observation of the results from run A led to a decision to use the less polar eluent for run B to allow better chromatographic separation of fractions 3 and 4.

Due to cost limitations, the four fractions from run B only were recovered from the TLC plate silica gel matrix by methylene chloride solvent extraction. Extraction of fraction 1 (near the origin on the TLC plate) with dichloromethane resulted in a biphasic liquid extract. These two phases underwent additional extractions, and similar fractions were combined. Extraction of fractions 2, 3, and 4 resulted in single compounds. Concentration of fraction 4 resulted in a deeply colored purple solid. All other fractions were white solids. These four extracts were analyzed gravimetrically (Table 4).
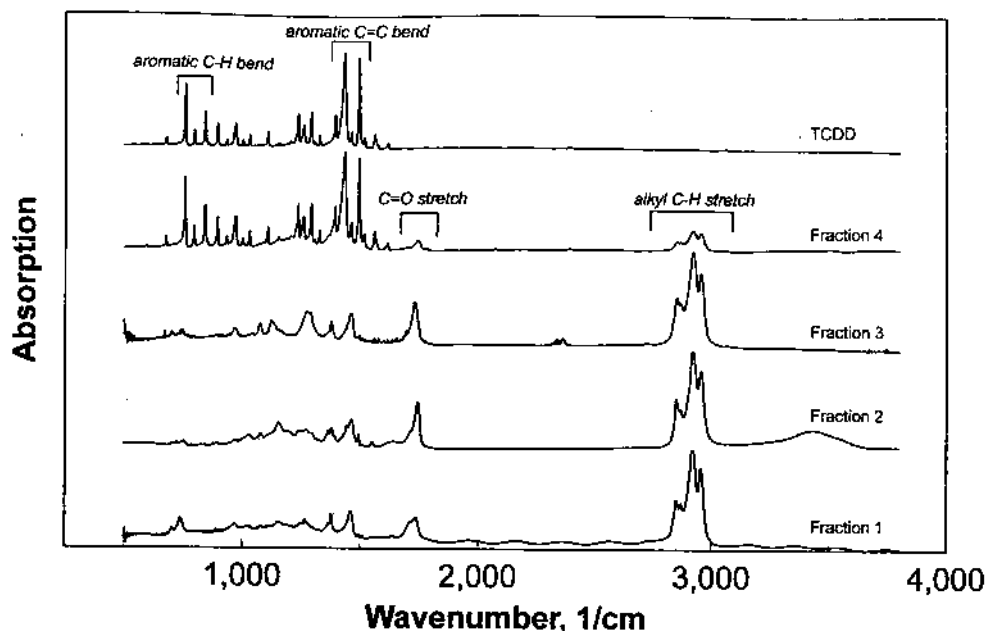
FIGURE 7. IR spectra of Table 3 product extracts and the TCDD reference.

TABLE 4. Gravimetric Analysis of Run B Products

fraction	mass (mg)
1	1.33
2	0.40
3	0.51
4	2.14
total	4.38
initial mass	4.08
% recovered	107

It is important to note that the extracts provide excellent recovery (107%) of the mass applied to the plate, implying that all of the TCDD that had been delivered to the sorbent (4.08 mg) and impinger (none detected) was recovered as products. Sample 4 faded from deep purple (suggesting a highly conjugated double-bonded compound) to white during the course of the gravimetric analysis, likely indicating the occurrence of photochemical reactions.

The four fractions identified in Table 4 along with 1,2,3,4-TCDD were subjected to infrared (IR) spectroscopy. Figure 7 presents the IR spectra for these materials.

A reference IR spectrum for 1,2,3,4-TCDD was not located. It is, however, very similar in character to Sadtler reference spectra 28798 K and 33034 K, which are 2,7-dichlorodibenzo-p-dioxin and dibenzo-p-dioxin, respectively. The two main peaks of TCDD, at 1435 and 1495 cm^{-1}, are assigned to out-of-plane, carbon—carbon, aromatic ring bending vibrations. The third main peak, 755 cm^{-1}, is assigned to out-of-plane, carbon—hydrogen, bending vibrations for four adjacent hydrogens on fused aromatic rings.

Fraction 4's IR spectrum is very similar to that of 1,2,3,4-TCDD, including the 1435, 1495, and 755 cm^{-1} bands assigned to aromatic ring bending vibrations for TCDD, but it also shows the addition of an aliphatic CH stretch (~2900 cm^{-1}) and carbonyl stretch (1700 cm^{-1}).

The IR spectra of fractions 1, 2, and 3 are similar, though not identical. Aliphatic CH stretch is the most important characteristic of these spectra, and all display carbonyl stretching bands in the 1710—1750 cm^{-1} region. The three primary peaks of 1,2,3,4-TCDD (1435, 1495, and 755 cm^{-1}, aromatic ring bending bands) are absent or minimal for these three fractions. The absence of these peaks indicates that these products result from the complete breakdown of the aromatic character.

Proton NMR data were collected for all four fractions and the parent 1,2,3,4-TCDD. As expected, the spectrum of 1,2,3,4-TCDD consists of a singlet in the aromatic region (magnetic field strength, $\delta = 7.01$ ppm). Because deuterated CDCl$_3$ was the solvent used for the NMR experiments, minor contaminants were expected (and found) for CHCl$_3$ ($\delta = 7.27$ ppm) and water ($\delta = 1.27$ ppm). Due to the small quantities of material available for the TLC fractions, these two contaminant peaks dominate the spectra of these samples.

The NMR data support the conclusions drawn from the IR data. The major peak for fraction 4 is at $\delta = 7.01$ ppm, which suggests that the benzylic ring remains intact in this sample. This aromatic peak is completely absent from fractions 1 and 2; it is a minor constituent of fraction 3. The presence of only minor or no aromaticity in fractions 1—3 is contradictory to previously mentioned GC results but is not entirely unexpected since the parent ion is often not observed during electron impact ionization experiments. New NMR peaks are found in the polar region ($\delta = 4.12$ ppm) and in the aliphatic region ($\delta = 0.8-2.5$ ppm). The peak at $\delta = 4.12$ ppm is found in samples 1, 2, and 3 and may represent a phenolic proton, but this is not conclusive. The position of a phenolic proton is strongly dependent upon concentration and also on the presence of hydrogen bonding groups.

Low-resolution, direct-probe electron impact mass spectroscopy (DPMS) was performed on these same fractions. The major feature of the spectra from fractions 1, 2, and 4 is a m/z of 320 cluster (the same molecular weight as TCDD), demonstrating a Cl$_4$ isotopic abundance pattern. For fraction 4, this pattern is distorted, apparently by a loss of hydrogen. The spectrum of fraction 3 has a possible parent ion at m/z = 307. This spectrum exhibits no isotopic evidence of Cl content. None of these electron impact spectra show evidence of higher molecular weight than TCDD. These latter two findings are unlike prior GC results (above) but may be a result of breaking down the parent ion with the high strength ionization technique used or from analyzing products from different experimental runs at different conditions.

Chemical ionization (CI) mass spectrometry techniques were applied only to fraction 4 due to limited sample quantities of the other fractions. Positive chemical ionization revealed a cluster at m/z = 349, a value higher than obtained with DPMS, suggesting that the DPMS method fractured the parent ion. Isotopic abundance patterns suggest that this is a Cl$_3$ peak. Negative chemical ionization revealed peaks at

$m/z = 334$ and 355, again larger than obtained with DPMS. Here again the isotopic abundance patterns suggest Cl_3 for the 334 peak and Cl_5 for the 355 peak.

High-resolution mass spectroscopy (HRMS) was performed on the $m/z = 355$ peak to determine empirical formulas. The resulting calculations on $m/z = 354.861375$, 356.858532, and 358.854986 are consistent with an empirical formula of $C_{12}H_4O_2Cl_5$. The unsaturation index for this empirical formula is 8.5, the integer value indicating the number of multiply bonded carbons (signifying the presence of rings, double-bonded C, or triple-bonded C), and the fractional remainder indicating incomplete bonding for the $m/z = 355$ ion. The latter suggests that the ionization technique has fragmented the original parent ion into a compound of lower molecular weight. HRMS on the $m/z = 334$ peak resulted in calculations for $m/z = 333.905178$ and 337.906689, which are consistent with an empirical formula of $C_7H_{11}O_4Cl_5$. The unsaturation index for this formula is 0, suggesting that this is a saturated aliphatic. Finally, HRMS on the $m/z = 349$ peak resulted in calculations for $m/z = 348.930808$ and 350.929687, which are consistent with $C_{14}H_9O_2Cl_4$. The unsaturation index for this formula is 8.5, again suggesting multiply bonded carbons and fragmentation of the parent ion.

With unsaturation indices that are fractional, neither $m/z = 355$ nor $m/z = 349$ can be the intact parent molecular ion for fraction 4. Similarly, the compound at $m/z = 334$ cannot be the parent molecular ion since there is no logical neutral loss that can explain a transition between the fully saturated fragment $C_7H_{11}O_4Cl_5$ and the TCDD aromatic ion $C_{12}H_4O_2Cl_4$ at 320. Therefore, the parent molecular ion for fraction 4 must be above 355 amu. The presence of fused ring structures related to 1,2,3,4-TCDD and large saturated strings implies that the molecular weight of fraction 4 is much larger than 320 and may be as large as the sum of the aromatic and saturated fractions.

The ability of the gravimetric analyses to achieve mass balance with the input TCDD (and the inability to find any volatile compounds with Tenax and Amberlite) supports the GC/MS findings that TCDD reacts with the $Ca(OH)_2$ (and CaO) and suggests that the products of reaction have all been accounted for. Tentative identification of some reaction products is provided, further supporting the role of Ca-based sorbents to participate in the reactive alteration of the TCDD structure. While these reaction products likely vary with reactor conditions, the products identified in our work remain multiply chlorinated; this is supported by extended GC/MS and CI/HRMS data. The high product retention times of the extended GC analysis, the IR evidence of a combined aromatic and aliphatic product, and the CI/HRMS results suggesting product fragmentation to compounds of MW = 320−355 all imply that an unstable dimerization of the 1,2,3,4-TCDD occurs, followed by progressive cleavage of the benzene rings in the TCDD structure. Fraction 4 represents a partially cleaved but mostly aromatic product, while fractions 3, 2, and 1 exhibit progressively more cleavage to aliphatic groups. The mechanism of the reaction between vapor-phase TCDD and $Ca(OH)_2$ (and CaO) and, specifically, the source of hydrogen for the increased aliphatic nature remain unanswered.

Literature Cited

(1) Kilgroe, J. D.; Nelson, L. P.; Schindler, P. J.; Lanier, W. S. Combustion Control of Organic Emissions from Municipal Waste Combustors. *Combust. Sci. Technol.* **1990**, *74*, 223−244.

(2) U.S. EPA. *Standards of Performance for New Stationary Sources and Emission Guidelines for Existing Sources: Municipal Waste Combustors*; 40 CFR Part 60, Dec 19, 1995.

(3) Einhaus, R. L.; Honarkhah, I.; Erickson, P. M. *Fate of Polychlorinated Biphenyls (PCBs) in Soil Following Stabilization with Quicklime*; U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory: Cincinnati, OH, Sep 1991; EPA/600/2-91/052 (NTIS PB92-114487).

(4) Erickson, P. M.; Einhaus, R. L.; Honarkhah, I. Laboratory Study of Interactions Between Polychlorinated Biphenyls and Quicklime. In *Proceedings: 18th Annual RREL Research Symposium*; U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory: Cincinnati, OH, Apr 1992; EPA/600/R-92/028 (NTIS PB92-166859).

(5) Koper, O.; Li, Y.-X.; Klabunde, K. J. Destructive Adsorption of Chlorinated Hydrocarbons on Ultrafine (Nanoscale) Particles of Calcium Oxide. *Chem. Materi.* **1993**, *5* (4), 500−505.

(6) Li, Y.-X.; Li, H.; Klabunde, K. J. Destructive Adsorption of Chlorinated Benzenes on Ultrafine (Nanoscale) Particles of Magnesium Oxide and Calcium Oxide. *Environ. Sci. Technol.* **1994**, *28* (7), 1248−1253.

(7) Rghei, H. O.; Eiceman, G. A. Adsorption and Thermal Reactions of 1,2,3,4-Tetrachlorodibenzo-p-dioxin on Fly Ash from a Municipal Incinerator. *Chemosphere* **1982**, *11* (6), 569−576.

(8) Rghei, H. O.; Eiceman, G. A. Adsorption and Thermal Reactions of Dibenzo-p-dioxin and 1-Chlorodibenzo-p-dioxin on Fly Ash from Municipal Incinerators. *Chemosphere* **1984**, *13* (3), 421−426.

(9) Dougherty, R. C.; Collazo-Lopaz, H. Reduction of Organochlorine Emissions from Municipal and Hazardous Waste Incinerators. *Environ. Sci. Technol.* **1987**, *21*, 602−604.

(10) Ross, R. A.; Lemay, R. *Destroying Halogen Containing Organic Compounds.* European Patent 184342 A1, June 11, 1986.

(11) Ross, R. A.; Lemay, R. Efficiencies of Aluminum, Magnesium, and Their Oxides in the Destruction of Vapor-Phase Polychlorobiphenyls. *Environ. Sci. Technol.* **1987**, *21* (11), 1115−1118.

(12) Sedlak, D. L.; Dean, K. E.; Armstrong, D. E.; Andren, A. W. Interaction of Quicklime with Polychlorobiphenyl-Contaminated Solids. *Environ. Sci. Technol.* **1991**, *25* (11), 1936−1940.

(13) Meta Environmental, Inc. *Treatability of PCB Contaminated Soils with Quicklime (CaO)*; Final report TR 101778, Research Project 2879-12; Union Electric Company and Electric Power Research Institute, Inc.: Palo Alto, CA, Nov 1992.

(14) Quinn, A. Final Results Available on Quicklime Treatment for PCB-Contaminated Soils. *Land Water Qual. News* **1992**, *6* (4).

(15) Gullett, B. K.; Lemieux, P. M.; Dunn, J. E. Role of Combustion and Sorbent Parameters in Prevention of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran Formation during Waste Combustion. *Environ. Sci. Technol.* **1994**, *28* (1), 107−118.

(16) *Method 0030, Volatile Organic Sampling Train, Test Methods for Evaluating Solid Waste, Volume II: Field Manual Physical/Chemical Methods*, 3rd ed.; EPA-SW-846 (NTIS PB88-239223); U.S. Environmental Protection Agency: Washington, DC, 1986.

(17) *Method 0010, Modified Method 5 Sampling Train, Test Methods for Evaluating Solid Waste, Volume II: Field Manual Physical/Chemical Methods*, 3rd ed.; EPA-SW-846 (NTIS PB88-239223); U.S. Environmental Protection Agency: Washington, DC, 1986.

(18) *Method 8270, Gas Chromatography/Mass Spectrometry for Semivolatile Organics: Capillary Column Technique, Test Methods for Evaluating Solid Waste, Volume IB: Laboratory Manual Physical/Chemical Methods*, 3rd ed.; EPA-SW-846 (NTIS PB88-239223); U.S. Environmental Protection Agency: Washington, DC, 1986.