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Reduction of Polychlorinated Dibenzodioxins and Dibenzofurans in Contaminated Muds by Mechanically Induced Combustion Reactions

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Some selected results are reported from an ongoing study concerning mechanochemical dehalogenation reactions carried out under autopropagating high-temperature regimes. Our work shows that instantaneous burning reactions can be ignited in highly exothermic systems involving chloroorganics when subjected to intensive mechanical treatments. A reference trial using calcium hydride−hexachlorobenzene is first presented. No residual traces of the organohalide compound were found in the reacted powders or in the gaseous phase sampled from the headspace of the milling reactor. The solid products of the reaction were restricted to CaHCl and $CaCl_2$ salts and graphite. Similar combustion-like phenomena were observed when contaminated mud samples were added to initial reactants. The contaminated mud was obtained from a waste site and contained traces of polychlorodibenzodioxins and polychlorodibenzofurans. It was observed that an effective chemical oven was created which caused the thermochemical breakdown of the hazardous compounds. A transformation yield greater than 99.6% was obtained with a decrease of the toxic equivalent concentration from 2492 to 0.788 μg/kg. Unlike conventional incineration methods, the mechanically induced burst processes run under a strictly confined environment and controlled conditions.

Introduction

Disposal of toxic chemicals such as polychlorinated biphenyls (PCBs), chlorinated pesticides, and polychlorinated dibenzodioxins (PCDD) and -furans (PCDF) has become a major problem for our technology (*1*−*3*). Traditional oxidative degradation, such as incineration in waste combustors, represents a significant environmental hazard since it can often lead to even worse congeners (*4*, *5*). Alternative remedy technologies have not been as effective as incineration and have met only limited success (*6*). Basic research therefore continues in the development of new disposal methodologies.

A mechanochemical degradation route was developed by Rowlands et al. (*7*). Following this line of research, we described the mechanochemical reduction of organochlorines carried out over ionic hydrides in high energy impact ball mills (*8*, *9*). The reaction rates were found to be determined by the intensity of the mechanical treatment. In the specific case of solid hexachlorobenzene, a self-accelerating or explosive-like behavior was observed beyond a milling intensity threshold (*9*), which led to an instantaneous transformation of the reactants to hydrogen, graphite, calcium halide, and/or the calcium hydride-halide mixed salt. Such combustive behavior was primarily connected with the inherent highly exothermic character of these reactions and with the ultimate limit of the reactant stability under progressively induced structural deformations. Two points are of concern here; a very high local temperature is achieved during reaction, and the adiabatic temperature (*10*), which determines the maximum local temperature of the powder, was calculated to be approximately 2890 K (*9*). In addition to this, the combustive-like region extends to compositions with a large excess of calcium hydride. These qualities prompted us to exploit the heat released at the combustive event to create a chemical oven. Our intention was to treat difficult systems, for instance, contaminated soil or sediment and mud. Real samples, containing PCDD and PCDF traces, were obtained from an actual waste site for testing. The aim of this paper is to show that such materials can be efficiently handled under combustive regimes when mixed with a primer mixture such as hexachlorobenzene and calcium hydride and that the contaminants are burnt by the heat produced by the principal reactants.

Experimental Section

Mechanical Treatment. The milling reactor consisted of a hollow hardened-steel cylinder, 3.7 cm internal diameter and 5.7 cm high, equipped with leak-proof valves. The reactor was clamped in a milling device (Spex Mixer-Mill model 8000) swinging at 875 rpm along a three-dimensional course. A single hardened-steel milling ball was used. As the mill operated, the ball was released inside the cylinder and, at each impact, its kinetic energy was transferred to the trapped layer of powder. A detailed account of the procedure and protocols we have developed to determine the impact energy, E, and the milling intensity, I, has been reported elsewhere (*11*). E (joule/hit) is defined as $^1/_2mv^2$, where v is the relative velocity of the colliding ball and m its mass. I (watt) is obtained by multiplying E by the number of collisions per second.

High-temperature combustion phenomena occurring under milling treatments are characterized by two distinguishing parameters: the sharp increase of the reactor vial temperature, ΔT, and the milling time at which the rapid temperature rise is registered, referred to as the ignition time, t_{ig}. As shown later, the first parameter, ΔT, can be related to the reaction heat released at the combustion-like event, whereas the product between t_{ig} and the milling intensity, I, gives the total amount of mechanical energy delivered to the reactants (*9*). Most of this energy is dissipated as heat while another part is utilized in the powder fragmentation, in defect generation, and to increase the particle contact area. This latter effect favors intermixing on a molecular level and ultimately rises the excess free energy to a threshold beyond which the process spreads spontaneously. In the present work the temperature of the reactor was continuously monitored during milling by a thin lamella-shaped Pt resistance thermometer fixed, under an insulating cover, on the outside surface of the reactor.

Reagents. CaH_2 (95%, −4 + 40 mesh) and C_6Cl_6 (99%) were purchased from Aldrich. The main hexachlorobenzene impurities were benzene and the isomers of bi-, tri-, tetra-, and pentachlorobenzenes.

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TABLE 1. Mechanochemical Trials, Mixture Composition, and Reaction Parameters

trials	mixture components	composition (g)	composition (10^2 mol)	I^a (W)	$t_{ig}{}^b$ (s)	ΔT^c (K)	ΔU^d (kJ/mol)
reference	$CaH_2 + C_6Cl_6$	2.50-1.88	5.9-0.66	3.48	7785	29.6	1765.6[e]
Md-a	CaH_2 + mud	2.50-0.50	5.9-	3.48			
Md-b	$CaH_2 + C_6Cl_6$ + mud	2.50-1.88-0.50	5.9-0.66-	3.48	8430	31.7	1.657[f,g]
Md-c	$CaH_2 + C_6Cl_6$ + mud	4.13-4.65-1.0	9.83-1.63-	4.40	3435	78.1	2.025[f,g]

[a] Milling intensity. [b] Ignition time. [c] Instantaneous increase of the reactor temperature. [d] Constant-volume reaction heat. [e] Per mole of C_6Cl_6. [f] Per gram of mud. [g] Calculated from the difference of the ΔT values with respect to the reference trials; see text.

The contaminated powders we tested were generated in an industrial wastewater treatment plant for chloroorganic solutions.

Procedure, Chemical Analysis, and Instrumentation. Powder batches of the hexachlorobenzene and/or contaminated material were loaded, with suitable quantities of the CaH_2 substrate, into the reaction vial under controlled argon atmosphere. At the end of the milling runs, the gaseous products were transferred from the headspace of the milling reactor to an initially evacuated canister and analyzed by following EPA method TO-15 (*12*). The reacted mixtures were then removed from the milling reactor and subjected to chemical and physicochemical characterization. Special attention was paid to determine tetra- (T) through octa- (O) dibenzo-*p*-dioxins (CDDs) and -dibenzofurans (CDFs) by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS), following EPA method 1613/94 *(13*). The highly toxic 17 2,3,7,8-substituted CDDs/CDFs may be determined by this method, and the determination of the other congeners is also possible. The sample was spiked with 15 labeled 2,3,7,8-substituted CDDs/CDFs and was extracted for 24 h using toluene. After extraction, sample cleanup included back-extraction with acid and base, and allumina, silica gel, Florisil, and activated carbon chromatography. CDDs and CDFs were separated by HRGC (Restek Rtx-5MS 60 m, 0.25 mm i.d., and Restek Rtx-2330 60 m, 0.25 mm i.d., columns were used) and detected by a high-resolution (≥10 000) mass spectrometer (MAT 95s − Finnigan). The 2,3,7,8-TCDD toxicity equivalents (I-TEQ) of CDDs and CDFs present in the sample were calculated using a NATO I-TEF method *(14*). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (I-TEF) to each of the 15 2,3,7,8-substituted CDDs and CDFs and to OCDD and OCDF. The 2,3,7,8-TCDD equivalent of the CDDs and CDFs present in the sample was calculated by summing the I-TEF values multiplied by their concentration for each of the 17 compounds.

Powder samples were also characterized by conventional X-ray diffraction (XRD) analysis.

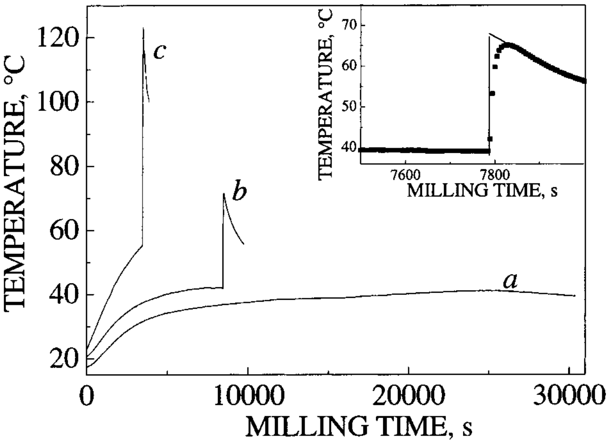

FIGURE 1. Trends of the milling reactor temperature in the course of milling runs carried out with mixtures of contaminated mud and CaH_2 (lower pattern a) or with mud plus CaH_2 and C_6Cl_6 (b and c). Curve c has an initially higher gradient due to the increased impact energy. Traces have been shifted to avoid overlapping. Inset: temperature increase of the reactor vial observed during the $CaH_2-C_6Cl_6$ trial run as reference. The onset of the sharp temperature rise marks the ignition time of the reaction. The correct ΔT value was obtained by extrapolating the decreasing trend of the temperature back to the ignition time.

Results and Discussion

The $CaH_2-C_6Cl_6$ Reference Trial. The reaction of CaH_2 with C_6Cl_6 was employed to ignite the contaminated mud batches. Full details on this reaction have already been reported (*8*, *9*). For the sake of comparison we present the essential combustive features of the mixture used: 2.505 g of CaH_2 with 1.885 g of C_6Cl_6, corresponding to a CaH_2/C_6Cl_6 molar ratio of about 9. Further data are presented in Table 1 together with the composition of the other specimens studied and the related milling parameters. The trace of the vial temperature during the milling treatment of the primer mixture is shown in the inset of Figure 1. A ΔT of 29.6 K was obtained at the brink of the temperature jump observed at an ignition time of 7785 s. According to previously reported procedures *(9*), the ΔT value is related to the reaction heat evolved during the combustive process. The reactor vial was regarded as a bomb calorimeter, and adiabatic conditions were assumed as the time scale of the event was short. Thus, considering the heat capacity of the vial and ball system (equal to 394.2 J/K), a reaction heat, ΔU, of about 1766 kJ/mol was obtained from the experimental ΔT value quoted above. Considering that the contribution to the reaction heat of the constant-volume running-mode term is negligible, the result agrees satisfactorily with the reaction enthalpy for the following transformation paths:

$$6CaH_2 + C_6Cl_6 \rightarrow 6CaHCl + 6C + 3H_2 \qquad (\Delta H = -1804.6 \text{ kJ/mol}) \quad (1)$$

$$3CaH_2 + C_6Cl_6 \rightarrow 3CaCl_2 + 6C + 3H_2 \qquad (\Delta H = -1709.6 \text{ kJ/mol}) \quad (2)$$

Moreover, in agreement with the end products forecast by the stoichiometry examined here, graphite, $CaCl_2$, and a predominant quantity of CaHCl were found in the XRD pattern of the reacted powder. No residual hexachlorobenzene was detectable. Hydrogen and methane were the main gaseous compounds at the end of the degradation process. Minor quantities of other volatile organic compounds were measured and are similar to those reported in Table 3.

The Case of the Contaminated Mud. Specimens, directly sampled from the treatment basin, were dried for 6 h at 393 K under argon and subjected to conventional powder characterization methods. Na (23.9 wt %), Mg (1.3 wt %), Al (3.0 wt %), Si (5.3 wt %), P (1.4 wt %), Cl (10.2 wt %), K (0.6 wt %), Ca (19.5 wt %), Fe (34.0 wt %), and Zn (0.17 wt %) and Cr (50 ppm), Mn (330 ppm), Ni (750 ppm), Cu (310 ppm), and Pb (795 ppm) were identified by electron probe microanalysis and atomic absorption spectroscopy, respectively. The main compounds characterized by diffraction methods were $CaCO_3$, NaCl, and FeOOH. As for the chloroorganic

TABLE 2. CDD and CDF Contaminants in the Mud Subjected to Milling Treatment[a]

	as received (μg/kg)[b]		after combustion (μg/kg)[c]	
	content	I-TEQ[d]	content	I-TEQ[d]
Polychlorodibenzo-*p*-dioxins				
2,3,7,8 -TCDD	852.6	852.6	0.113	0.1128
1,2,3,7,8-PCDD	1440.6	720.3	0.828	0.4141
1,2,3,4,7,8-HCDD	774.3	77.4	0.261	0.0261
1,2,3,6,7,8-HCDD	485.4	48.5	0.169	0.0169
1,2,3,7,8,9-HCDD	819.6	82.0	0.289	0.0289
1,2,3,4,6,7,8-HPCDD	578.9	5.8	<0.002	0.0000
1,2,3,4,6,7,8,9-OCDD	797.1	0.8	0.420	0.0004
other PCDD	80.9		<0.002	
Polychlorodibenzofurans				
2,3,7,8-TCDF	974.5	97.5	0.272	0.027
1,2,3,7,8-PCDF	779.0	39.0	0.203	0.010
2,3,4,7,8-PCDF	726.1	363.0	0.159	0.079
1,2,3,4,7,8-HCDF	776.9	77.7	0.248	0.025
1,2,3,6,7,8-HCDF	646.2	64.6	0.225	0.023
2,3,4,6,7,8-HCDF	579.2	58.0	0.215	0.022
1,2,3,7,8,9-HCDF	1.4	0.1	<0.002	0.000
1,2,3,4,6,7,8-HPCDF	5.9	0.1	0.099	0.001
1,2,3,4,7,8,9-HPCDF	440.4	4.4	0.198	0.002
1,2,3,4,6,7,8,9-OCDF	188.1	0.2	0.144	0.000
other PCDF	50.7		0.294	
	total TEQ 2492		total TEQ 0.788	

[a] EPA method 1613/94. [b] Per kilogram of mud. [c] Per kilogram of solid product. [d] International toxic equivalent concentration.

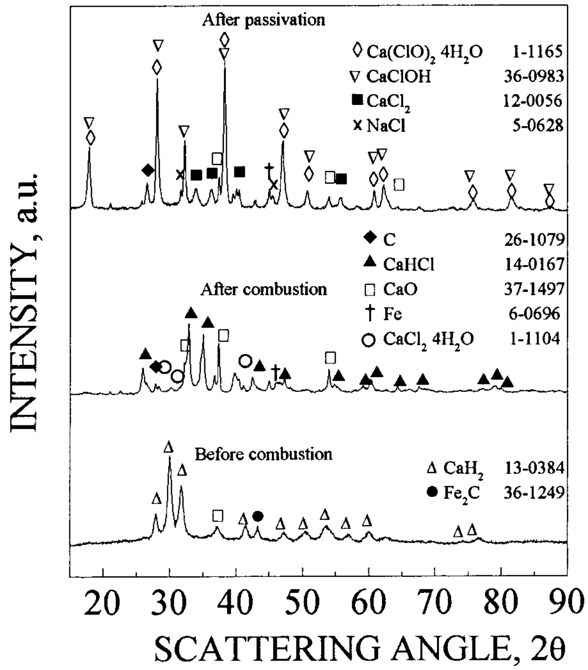

FIGURE 2. Cu Kα XRD patterns of mud−CaH_2−C_6Cl_6 powders before and after the combustion reaction (Md-c trial). The upper pattern refers to the same reacted powders after an air−argon flux. Symbols mark the peak positions as given by the quoted JCPDS reference cards (*15*).

contaminants, Table 2 gives the CDD and CDF content in the material received.

Initial tests were performed using only calcium hydride and the contaminated mud, utilizing different ratios and under different milling conditions. No observable combustion-like reaction was observed, and significant transformation of the organochlorine compounds was not achieved. One experiment is presented as curve a in Figure 1 for a milling time up to 3.0×10^4 s, pertaining to a mud load of 0.5 g milled with 2.5 g of CaH_2 (trial Md-a). The lack of combustive behavior can be related to the poor exothermic qualities of the CaH_2−mud system inadequate to reach self-propagating regimes.

Conversely, combustion-like reactions were observed when the contaminated mud was milled with a CaH_2−C_6Cl_6 mixture as a primer. As shown in Figure 1, important temperature jumps characterize the temperature traces b and c which refer to two ternary mixtures quoted in Table 1 as Md-b and Md-c, respectively. In the former, 0.5 g of mud was milled with 2.50 g of CaH_2 and 1.88 g of C_6Cl_6, and in the latter, 1 g of mud was tested with 4.13 g of CaH_2 and 4.65 g of C_6Cl_6. From trace b, an ignition time of 8430 s and a ΔT of 31.7 K were recorded, close to the corresponding parameters obtained for the reference mixture—a difference of 2.1 K was observed in the ΔT values. As for the Md-c mixture, the milling intensity was increased from 3.48 to 4.4 W. t_{ig} dropped to 3435 s, and this result fits well with our previous findings, according to which ignition times rapidly decrease by increasing the impact energy (*9*). ΔT reached 78.1 K, 5.1 K higher with respect to that of 73 K observed in a binary mixture of CaH_2 (4.13 g) and C_6Cl_6 (4.65 g) tested in parallel. The mud's contribution to the total reaction heat was tentatively calculated from the temperature differences above (2.1 and 5.1 K) and gave an average value of about 1841 J per gram of added mud. A straightforward correlation of this quantity with the organohalide content in the contaminated mixture is not possible. Several inorganic compounds are present in the mud, and possible cross-reactions between them may have occurred. This is also suggested by some intermediate phases observed in the XRD pattern of powders taken from the reactor before combustion. As can be observed in the lowest pattern of Figure 2, which refers to the Md-c trial, $CaCO_3$ decomposes in the course of the milling treatment giving rise to CaO, whereas FeOOH transforms into the Fe_2C iron carbide. In the pattern collected immediately after combustion, and also shown in Figure 2, diffraction lines pertain to CaHCl, $CaCl_2{\cdot}4H_2O$, CaO, Fe, and graphite. To conclude the analysis of the XRD data, we show the upper pattern in Figure 2 which refers to the reacted mixture after exposure to air under an air−argon flux. This pattern shows important reflections from calcium hypochlorite, $Ca(ClO)_2{\cdot}4H_2O$, and from calcium chloride hydroxide, CaClOH. $CaCl_2$, graphite, and NaCl are the other phases present.

The results of a mass balance involving the CDDs and CDFs proved inconclusive. This is primarily due to the relatively large quantities of principle elements in the starting materials (Cl in hexachlorobenzene, NaCl and $CaCO_3$ in the mud) in relation to the contaminants in the sample. The amount of chlorine in the primer reactant is 6 orders of magnitude larger than the chlorine content in the CDDs and CDFs, whereas large carbon dioxide concentrations are produced from the decomposition of $CaCO_3$, present in large quantities in the mud. Similar conditions are met when hydrogen is considered. These circumstances forced us to consider the contaminant content before and after reduction. The residual CDDs and CDFs in the solid products at the end of the Md-c trial are listed in Table 2. The final concentrations were measured to be 2.08 μg/kg and 2.05 μg/kg, respectively. When the actual amount of mud in the starting ternary mixture was considered, a transformation yield greater than 99.6% was obtained. The total TEQ concentration decreased from 2492 to 0.788 μg/kg. The main organic byproducts and their concentrations are listed in Table 3. Some of these compounds were already present in the starting hexachlorobenzene in much higher quantities (at. % level). The total organochlorines conversion, also considering the C_6Cl_6 reactant, resulted in better than 99.9999%.

TABLE 3. Concentration of Volatile Chloroorganic Products Formed in the Mechanically Induced Combustion of a $CaH_2-C_6Cl_6$-Contamined Mud Mixture[a]

compd[b]	concn (μg/m^3)[c]
dichloromethane	67
chloroform	101
benzene	2542
toluene	155
chlorobenzene	120
ethylbenzene	44
m,p-xylene	91
styrene	12
o-xylene	38
1,3,5-trimethylbenzene	34
1,2,4-trimethylbenzene	131
1,3-dichlorobenzene	49
1,4-dichlorobenzene	36
1,2-dichlorobenzene	88
1,2,4-trichlorobenzene	258

[a] EPA method TO-15. [b] Other: propane (1475), isobutane (432), 1-propene-2-methyl (47), *n*-butane (773), *n*-pentane (171), cyclopentane (62), *n*-hexane (88), cyclohexane (62). [c] 298 K, 760 mmHg.

The results show that a self-propagating combustion-like process could present a possible treatment of difficult materials. A very effective chemical oven is activated by the heat evolved. The consequent high temperatures reached in the reacting powders are capable of reducing the concentrations of chloroorganic compounds present in actual contaminated soils to the limit of detection. The pyrolysis of the organic components and the related charring processes involved are helped by the reductive properties of the CaH_2 substrate and by the thermodynamically favored exchange of hydrogen for chlorine in the primary reaction toward CaHCl or $CaCl_2$.

The use of mechanically activated self-combustion processes to deal with residual quantities of hazardous compounds has been shown to be feasible. The advantages over conventional incineration are obvious in that higher temperatures and extreme chemical reactivity levels can be achieved under carefully controlled conditions. In some cases the products need to be passivated; however, they can be easily checked before discharge into the environment.

The scaling up of a milling reactor for large technology seems unfeasible at the moment; however, some possible lines of inquiry have emerged. It is well known that conventional self-propagating exothermic reactions (SHS) (*16*, *17*) between particulate materials can be induced by instantaneous ignition methods, for instance, by heating the sample locally with a hot wire or an electrical spark or even a laser beam (*18*). These methods might have advantages over ball milling in terms of efficiency and industrial size processes (*19*). The results obtained with the concurrent use of both techniques and concerning dehalogenation processes similar to those explored here will be described in a forthcoming paper (*20*).

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