

Treatment of Complex Chemical Wastes with the Base Catalyzed Decomposition (BCD) Process

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During the 1980's, a chemical dechlorination process was developed to treat oils contaminated with PCBs. The reagent used in this process was prepared by combining polyethylene glycol with either potassium or sodium hydroxide. When heated to 90-100°C, a metal alkoxide (APEG) was produced which then displaced the chlorine atoms on chlorinated molecules. Following detailed laboratory studies with PCDD contaminated soils,¹⁻³ the APEG reagent was employed to treat PCB contaminated soils at sites located in Moreau, New York, and the Island of Guam in the Pacific. The Guam field test employed a 400 gallon mixer to treat 27 tons of soil which contained up to 4500 ppm of PCB. After treatment in the batch reactor for 4-6 hours at 135-150°C, the soil contained slightly more than 2 ppm of PCB. Retreating the soil reduced the concentrations of PCB congeners to less than 2 ppm⁴; the target objective.

After evaluating the results of the APEG field tests, laboratory studies were initiated to investigate superior alternatives to the APEG chemical treatment process. The objectives applied in developing an alternative process included:

1. Treatment procedures should be amenable to continuous processing
2. The process should be capable of treating soil agglomerates larger than 0.5 inch diameter
3. Less expensive sodium hydroxide should be used rather than the potassium hydroxide used previously
4. Polyethylene glycol should be eliminated from the process
5. The Treatment time period should be reduced
6. Other non-halogenated organic components of the waste should be removed, if possible from the matrix during processing
7. The reagent utilized should more effectively treat compounds with high degrees of halogenation
8. The reagents used should be non-hazardous and the waste stream resulting from the process should be sufficiently clean to permit disposal as non-hazardous materials.

Catalytic transfer hydrogenation, in which an organic reagent serves as a hydrogen donor, has been investigated in the present study as a process which could satisfy most of the treatment objectives listed above. Previous studies conducted by the U. S. EPA have demonstrated the effectiveness of this process for treating PCBs in laboratory scale experiments. A mixture of 1.0 g of Aroclor 1260, 50 mL of high boiling oil (318-387°C), 2.5 g of sodium hydroxide and 1.0 g of a proprietary hydrogen donor-catalyst were heated for a period of one hour at 320-330°C. The treated residue contained no detectable concentrations of the PCB congeners. Subsequent tests with PCB-contaminated soils demonstrated that the concentration of base in the treatment mixture was critical to the efficiency of the process. This process has been designated Base Catalyzed Decomposition (BCD).

The BCD process has been employed to treat high levels of PCBs in liquid formulations and in PCB-saturated wood and paper matrices from transformers. In these instances, 2 g of sodium hydroxide were added to the reaction vessel for each gram of PCB. Hydrogen needed for the dechlorination was provided by low cost #5 or #6 fuel oil. The proprietary catalyst was added to the reactor in an amount equivalent to 1% by weight of the waste and the mixture was heated to 340°C. For liquid mixtures, the concentration of Aroclor 1260 in the treated residual products was reduced to non-detectable levels within a period of two hours. PCB-contaminated wood and paper wastes were typically heated for six hours to reduce the concentration of Aroclor 1260 to a non-detectable level.

As part of a study to determine the effects of other variables on the efficiency of the BCD process, a series of laboratory experiments were conducted to treat a 2,4-D/2,4,5-T herbicide formulation which contained 33.4 ng/g of 2,3,7,8-TCDD. The ratio of the quantity of a high boiling oil added along with other reagents to the liquid herbicide was 1:1, 2:1 and 3:1 in three separate treatments. In the first reaction test, 10 mL of the high-boiling oil, 10 mL of the liquid herbicide, 8 g of sodium hydroxide and 2 g of catalyst were mixed and tested. In the second and third reactions, 20 mL and 30 mL, respectively, of the high boiling oil were added to the treatment vessel along with the other reagents in the same amounts as for the first reaction. Each of these mixtures was heated for three hours at 320-360°C, after which the residue remaining in the reactor and the distillate collected during the reaction were analyzed. Each of the three reactions reduced the concentration of 2,3,7,8-TCDD in the residual treated mixtures to a non-detectable concentration, as shown in Table 1. The concentrations of 2,3,7,8-TCDD found in the volatile distillates from each of these reactions are also shown in Table 1. Clearly, increasing the quantity of high boiling oil in the reaction mixture results in a decrease in the amount of 2,3,7,8-TCDD which is found in the distillate.

Presumably, increasing the quantity of oil increases the quantity of the hydrogen donor and accelerates the dechlorination reaction, thereby reducing the quantity of TCDD in the distillate. In addition, the larger quantity of oil may retain the TCDD in the heated reaction mixture better, so that other rate limiting reactions have a better opportunity to dechlorinate the molecule.

Previous treatment tests conducted in our laboratory with vermiculite which contained 2,4-D, 2,4,5-T and Silvex demonstrated that a somewhat different version of the BCD process effectively dechlorinates all of these herbicides. Combining 20 g of the contaminated vermiculite with 10 g of sodium bicarbonate and heating the mixture for 6 hours at 340-350°C reduced the concentration of the herbicides by 98-99%. This treatment also reduced the concentration of 2,3,7,8-TCDD in the vermiculite by 99.986%. A modification of the vermiculite treatment procedure was subsequently used to treat a PCP contaminated soil. In the latter test, a 50 g soil sample was combined with 13 g of sodium bicarbonate and 0.5 g of a catalyst. Initially the soil contained 94 ppm of PCP. After heating the mixture for two hours at 320-340°C the PCP could not be detected in the treated product at a detection limit of 3 ppm. The treatment of the contaminated soil using the BCD process resulted in a reduction of the PCP concentration by greater than 96%.

During the BCD reaction in an open reactor, water and other volatile components which are driven from the reaction mixture are collected, extracted, and then dechlorinated in a separate treatment sequence. In order to simplify the design of the process, experiments have recently been conducted using a high-pressure sealed reactor. This type of batch reactor completely contains the volatile components and the entire treatment occurs in a single step. These experiments were conducted with a one liter high pressure Hastelloy C reactor. Vermiculite was mixed with liquid herbicide to give a sample which contained 10.5 mg/g of 2,4-D, 33 mg/g of 2,4,5-T and 8.0 mg/g of Silvex. A 15 g portion of the highly contaminated vermiculite was combined with 300 g of sodium bicarbonate in the pressure reactor. The mixture was treated for 9 hours at 340-350°C and reached a maximum pressure of 2210 psi. None of the three herbicides could be detected in the treated sample and the concentrations of 2,4-D, 2,4,5-T and Silvex were reduced by >99.983%, >99.995% and >99.978% respectively. Additional studies employing the high pressure reactor are currently underway.

The results of several different laboratory BCD experiments are summarized in Table 2. It is evident that the BCD process can effectively treat a variety of complex matrices and is effective for several classes of halogenated pollutants. The simplicity and moderate cost of the BCD process make this process a viable and attractive alternative to the APEG treatment.

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Table 1

Concentration of 2,3,7,8-TCDD in the Residues and Distillates from a BCD-Treated Herbicide Mixture

Ratio of Herbicide to Oil in the Treatment	Quantity of 2,3,7,8-TCDD in Treated Mixture (ng)	Quantity of 2,3,7,8-TCDD in Distillate (ng)
1:1 Herbicide:Oil	ND(0.05)	1429
1:2 Herbicide:Oil	ND(0.06)	798
1:3 Herbicide:Oil	ND(0.25)	354

Table 2

Summary of Laboratory BCD Treatment Tests with Various Halogenated Materials

Treated Contaminant	Matrix	Concentration Prior to Treatment	Treatment Process	Percent Destruction
2,4-D	Vermiculite	10.5 mg/g	NaHCO ₃ Pressure Reactor	>99.983%
2,4,5-T	Vermiculite	33 mg/g	NaHCO ₃ Pressure Reactor	>99.995%
Silvex	Vermiculite	8.0 mg/g	NaHCO ₃ Pressure Reactor	>99.978%
PCP	Soil	94 µg/g	NaHCO ₃ /Carbon Glass Reactor	>96.1%
2378-TCDD	Vermiculite	4.14 µg/g	NaHCO ₃ Glass Reactor	99.986%
PCB (Araclor 1260)	Liquid	20,000 µg/g	NaOH/Fuel Oil/Catalyst Glass Reactor	>99.95%