

Conclusion

Various pre-tests were carried out to obtain the optimum conditions for maximum destruction efficiency of adsorbed organics. The temperature of flame front, carbon loss, and the changes in physical properties of carbon during COS were found to be strongly dependent on oxygen flow rate. The temperature reached was high enough to insure complete destruction of the organic chemicals. The carbon loss was controllable. The analysis of specific surface area after 3 successive COS cycles indicated that the adsorptive capacity of the carbon remains largely intact. The result was supported by batch adsorption experiments of regenerated carbons with PCB contaminated oil. The overall results obtained during the studies demonstrate that COS is a single step regeneration/destruction process, and could prove to be highly effective for the regeneration of spent carbon.

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Application of a Novel Carbon Regeneration Process for Disposal of APEG Treatment Waste

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The chemical waste treatment, APEG (alkali/polyethylene glycol) process has been shown to be effective for the dechlorination of PCBs in transformer oil. Considerable amount of PCBs, however, still remains in the waste exceeding the 25-50 ppm limit set by regulatory agency. A new thermal regeneration technology has been developed in our laboratory for disposal of hazardous organic wastes. Due to the limited oxidation of carbon surface through the reverse movement of flame front to oxidant flow, this technology was termed counterflow oxidative system (COS). Specially, the oxidant flow in the COS process is a principal parameter which determines the optimum conditions regarding acceptable removal and destruction efficiency of adsorbed organic wastes at minimal carbon loss. The COS process, under optimum conditions, was found to be very effective and the removal and destruction efficiency of 99.99% or better was obtained for residual PCBs in the waste while bulk ($\geq 90\%$) of carbon was recovered. Any toxic formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs) were not detected in the regenerated carbon and impinger traps. The results of surface area measurement showed that the adsorptive property of regenerated carbon is mostly reclaimed during the COS process.

Introduction

Modern society operates on electric power and a world without electric power is unthinkable. Transformers are integral components of electric power distribution system. The operation of these components is dependent on dielectric materials in the components. In the case of power transformers, the dielectric materials should possess a high dielectric constant and also be chemically and thermally stable. PCBs were found to possess these properties.^{1,2} However, due to the potential environmental threat and toxicity associated with PCBs,³⁻⁵ these chemicals in transform-

ers have been retrofilled with mineral oil or other dielectric fluids.⁶ Although the resulting transformers generally have small amounts of PCBs, falling between 100-2,000 ppm, these levels still exceed the USEPA (United States Environmental Protection Agency) mandated level of 25-50 ppm.⁷ Since the number of transformers is so numerous worldwide, the PCB contaminated dielectric fluids represent a significant environmental problem.

The disposal of PCBs has been a major area of concern. The approaches for this purpose have been addressed through incineration and chemical dechlorination. The high temperature incineration^{8,9} is straightforward. However, this

technology precludes recovery of reusable materials and forms toxic, environmentally persistent by-products under certain incinerator conditions. The most notable toxic compounds are polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs). PCDDs have been detected in the exhaust gases and particles of municipal solid waste incineration. PCDFs have also been found in residues from PCB fires and waste PCB fluid incineration.¹⁰ A chemical dechlorination method, known as the APEG (alkali/polyethylene glycol) process, has become the most frequently used treatment technology for decontamination of PCB-laden transformer oil.¹¹ Polyethylene glycol acts as both catalyst and nucleophile in the reaction with PCBs under basic conditions. Complete reaction with APEG and PCBs produces aryl polyglycols, the products of nucleophilic aromatic substitution, and forms an inert, common salt-sodium/potassium chloride. This method is generally effective, but somewhat cumbersome.

The alternative procedure is the use of activated carbon. We have demonstrated that activated carbon can be used for removing PCBs from mineral oil.¹² Still there arises a perplexing issue: what to do with PCB contaminated carbon. Ideally one would want a process that destroys PCBs leaving the carbon intact. A number of thermal regeneration technologies have been developed and used on a large scale to regenerate the spent carbon. One of the thermal technologies used for this purpose is wet air oxidation.^{13,14} This technology is, however, characterized by incomplete destruction of the adsorbed organic compounds and large consumption of heat energy. These unfavorable situations can largely be overcome by a carbon regeneration procedure termed counterflow oxidative system (COS). The COS process utilizes a flame front which propagates itself in a direction counter to the flow of oxidant. The flame front gasifies the carbon and adsorbed organics in a localized zone, consuming most of the available oxidant. The process shows a number of characteristics which make it suitable for the treatment of PCBs. The reaction temperature in the process is high enough to ensure destruction of PCBs because these chemicals are thermodynamically unstable at temperatures higher than 800 °C.¹⁵ No additional energy input except initial ignition is required. The carbon loss is controllable by changing the oxygen flow rate.

The present study was designed to examine efficiency of COS for destruction of residual PCBs in APEG treatment waste, to monitor the possible formation of toxic by-products such as PCDDs/PCDFs during the regeneration, and to evaluate characteristics of regenerated carbons.

Experimental

Characterization and Quantification of Residual PCBs in APEG Waste. The APEG waste sludge was obtained from Sea Marconi Technologies (Torino, Italy). One gram of waste was dissolved in 100 mL of methanol. A 2 mL aliquot of this solution was introduced into a silicagel chromatographic column to remove residual interferences and to fractionate PCBs. The column was eluted with 40 mL of methylene chloride. These fractionations were carried out with silicagel (Davisil, Grade 923, 80-100 mesh). Prior to its use with the sample, the silicagel was

rinsed three times with 300 mL acetonitrile/methylene chloride (v/v 40:60) in a 5 cm (i.d.) \times 50 cm long column. The cleaned silica-gel was air dried in a fume hood for 48 hours. It was then activated overnight at 130 °C oven. The activated silica-gel was allowed to cool to room temperature in a vacuum desiccator.

Separation of the PCBs of interest in the extracts was accomplished with a capillary gas chromatograph (Model 8500GC, Perkin Elmer Corp., Norwalk, CT) equipped with an electron capture detector (ECD). A 30 m \times 0.25 mm (i.d.) fused silica tubing with 95% methyl + 5% phenylpoly-siloxane stationary phase column (DB 5, Supelco, Inc., Bellefonte, PA) was used for chromatographic separation. The GC oven was temperature programmed through two step ramps, an initial fast ramp from 80 °C to 180 °C at 10 °C/min followed by a slower ramp rate of 3 °C/min to 265 °C. Helium and P-10 mixture (10% methane in argon) were used as the carrier gas. Stock solution was prepared at a nominal concentration of 1 mg/mL by dissolving 0.1 \pm 0.005 g of PCBs in 100 mL of iso-octane. The concentrations of calibration standards ranged over three orders of magnitude from 10 μ g/L-10 mg/L through dilutions of stock solution. Each calibration standard contained 50 μ g/L of pentachlorobenzene as the internal standard. The identification of PCBs in sample was accomplished by matching the relative retention time to that of pentachlorobenzene. The quantification of individual PCB congeners was carried out by peak measurement relative to external calibration standards.

Optimum Condition of COS. The effectiveness of the COS process is affected not only by the gradual loss of carbon during the regeneration, but also by efficient removal and destruction of adsorbed materials to make fresh carbon surface available for the further adsorption. The oxygen flow is a major parameter which determines the optimum conditions of COS process. The carbon loss and flame front temperature are affected by the oxygen flow. The rates of oxygen flow conducted at experimental scope were 60 mL/min, 120 mL/min, 350 mL/min, and 600 mL/min, respectively. The amount of carbon loss was determined gravimetrically. The flame front temperatures were directly measured with a thermocouple, Pt resistant thermometer, and an infrared temperature indicator. However, due to the transient nature of the flame front, these measurements proved difficult to reproduce. For this reason, an indirect measurement was obtained from the ratios of CO/CO₂ in the off-gases. The ratios were determined with a GC-TCD, by measuring the response relative to standard gas mixtures (CO, CO₂, H₂, CH₄, and O₂, Scott Specialty Gases, Inc., Durham, NC). The gases were separated with a carbosieve (60-80 mesh) packed column at 80 °C oven temperature. Helium was used as the carrier gas.

Removal and Destruction Efficiency of PCBs in APEG Waste. The APEG waste treatment was conducted with laboratory experimental scale. It consists of an oxidant inlet, a reactor tube, and a series of liquid impingers. A schematic diagram of COS set-up for disposal of PCBs is shown in Figure 1. A reactor was constructed with a 1 cm wide \times 30 cm long quartz tube with cajon O-ring caps. The oxidation was carried out primarily with oxygen. The flow of oxygen was controlled with a pressure regulator in series with a needle valve. The flow was monitored with a cali-

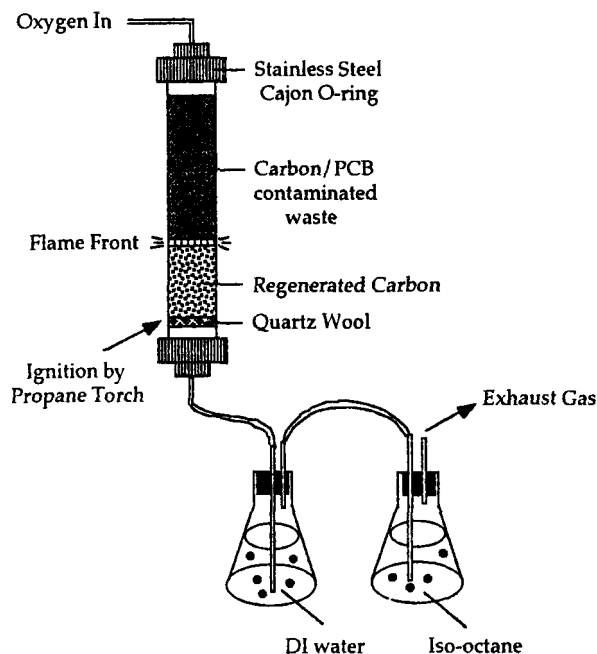


Figure 1. Schematic Diagram of COS Set-Up for Disposal of PCBs.

brated rotameter. The impinger traps were filled with deionized water and iso-octane. Each trap is allowed to trap HCl gas and PCBs/PCDDs/PCDFs, respectively.

The waste was mixed with activated carbon at five different ratios (1, 5, 10, 20, and 30 w/w %). Obviously, a higher waste loading is desirable if combustible efficiency can be maintained. Activated carbon (Darco, Granular, 20-40 mesh) was purchased from Aldrich. The mixture was placed in the reactor and ignited at the bottom of the reactor using a propane torch. The self-sustained flame front was generated, and moved counter to the oxygen flow, gasifying the carbon and adsorbed PCBs. The oxygen flow was stopped when the flame front reached the top of the carbon. After cooling, the regenerated carbon was withdrawn from the reactor. A portion of regenerated carbon was Soxhlet extracted with methylene chloride for at least 24 hours to remove strongly adsorbed PCBs. The extract was reduced to 2 mL by rotary evaporator. The PCBs were analyzed with a GC-ECD. The analysis of PCDDs/PCDFs were carried out with a capillary GC interfaced to a quadrupole mass spectrometer (Model 5970B, Hewlett Packard Corp.). The PCDDs/PCDFs standards were purchased from Ultra Scientific Inc., North Kingstown, RI. Chromatographic separations were achieved with a 25 m \times 0.25 mm (i.d.) fused silica column (DB-5, J and W Scientific Inc., Folsom, CA). The gas chromatographic oven temperature was ramped from 120 °C to 290 °C at 10 °C/min and then maintained for 5 minutes at 290 °C. The mass spectrometer was operated in the selected ion monitoring mode. The water trap was used for chloride determination. Hydrochloric acid was analyzed by an ion chromatograph (Model System 14, Dionex, Sunnyvale, CA) equipped with ion resin columns (separator and suppressor column). The samples were quantified by peak response relative to standard solution. The iso-octane trap was concentrated to 2 mL by rotary eva-

porator, and the PCBs and PCDDs/PCDFs were analyzed by GC and GC/MS.

Evaluation of Carbon Surface Characteristic.

The experiment involves measurement of change in such salient characteristic as surface area brought by the COS. Surface area measurement of regenerated carbons was carried out with the N₂ BET method. The analysis was performed on a Quantasorb QS-10 Surface Area Analyzer (Model QS-10, Quantachrome Corp., Syosset, NY).

Results and Discussion

Characterization and Quantification of Residual PCBs in APEG Waste.

The product of APEG reaction with PCBs in transformer oils is a fairly viscous solution containing substituted aromatic compounds, inorganic chloride salts, and/or residual PCBs. A batch of APEG treatment waste was characterized and quantified for PCB residue. The chromatographic profile of residual PCBs is presented in Figure 2. Residual PCBs in waste were no longer similar to the composition of Aroclor mixture. The APEG treatment was shown to be effective in reducing the concentration of highly chlorinated (≥ 5) PCB congeners. However, it was less effective in dehalogenating PCB congeners with four or less chlorine atoms. The concentration of residual PCB congeners was thus determined on the basis of percent contribution of individual PCBs to Aroclor 1242 (the mixture of PCBs composed of mostly 3 and 4 chlorine atoms on biphenyl frame) reported by Schulz *et al.*¹⁶ The total concentration of residual PCBs was approximated by aggregating the concentration of individual PCBs. The value was found to be 770 ppm. Such amount of PCBs still poses disposal problem. Since PCBs adsorb strongly to activated carbon, use of activated carbon will provide a viable means of management for the disposal. Its application is, however, limited due to high material and

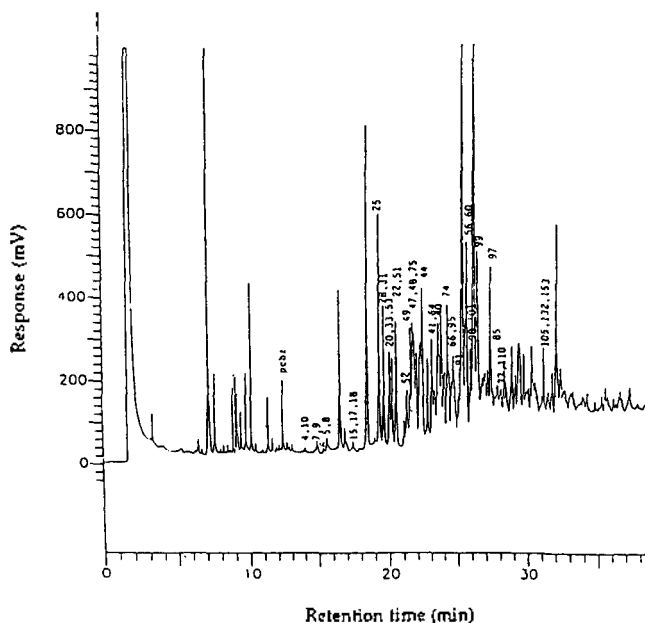


Figure 2. Chromatograms of Residual PCBs in Alkali/Polyethylen Glycol (APEG) Waste Sludge.

disposal costs. These two limitations can be coped with a COS regeneration procedure.

Optimum Conditions of COS. The COS process involved balancing two opposing conditions: minimization of carbon loss and maximization of the PCB destruction. The latter could be achieved by maintaining high temperature during the regeneration process. It was observed that carbon loss and flame front temperature were strongly dependent on oxygen flow rate. The carbon loss was in the range of 5% to 15% with changes in oxygen flow rate. The flame front temperature of COS was determined on the basis of relative concentration of the CO and CO₂. The values varied between 1,100 K and 1,900 K.

The temperature was calculated according to the following procedures. A known amount of carbon was placed in a quartz tube of cross-section A and length L . The number of moles of carbon per cm³ is $C_c = w/(12AL)$. In a section of this tube of length L , the carbon and oxygen initially at T will be converted to carbon(C), CO(g), and CO₂(g) at temperature T' , with loss of some of the carbon (Δn_c). All of the oxygen delivered at a volumetric flow rate (F , cm³/sec) and pressure P (atm) is assumed to be consumed. The amount of oxygen consumed depends on the total burn time. This calculation neglects oxygen which is present in the interparticle pore and intraparticle pore space at the beginning of the burn. The flame advances through this section at a linear burning rate (B , cm/sec). The time required is $t=L/B$. The volume of O₂ burned is: $V_{O_2} = Ft = FL/B$. Moles of O₂ burned are: $\Delta n_{O_2} = kFPL/BT$, where $k=0.001/0.08205=0.01219$ (molK/cm³atm). The ratio of carbon to oxygen burned is: $\Delta n_c/\Delta n_{O_2} = 2/(1+f)$, and $\Delta n_c = 2kFPL/BT(1+f)$. f =mole fraction of CO₂ in product stream. The total moles of carbon involved is $n_c = AC_cL$, so $\Delta n_c/n_c = 2kFP/AC_cBT(1+f)$. The process is $(n_c/\Delta n_c)C(s, T) + (1+f)O_2(g, T) \rightarrow fCO_2(g, T') + (1-f)CO(g, T') + [(n_c/\Delta n_c) - 1]C(s, T')$ and is assumed to occur adiabatically, so that

$$0 = f[\Delta_f H_{CO_2} + \int_T^{T'} C_{pCO_2} dT] + (1-f)[\Delta_f H_{CO} + \int_T^{T'} C_{pCO} dT] + [(n_c/\Delta n_c) - 1] \int_T^{T'} C_{pC} dT$$

with enthalpies of formation $\Delta_f H$ at T , which is taken as 298.15 K. The final temperature, T' , was estimated from enthalpies of formation and heat capacities of CO and CO₂ gas. Optimum condition was determined at a middle point

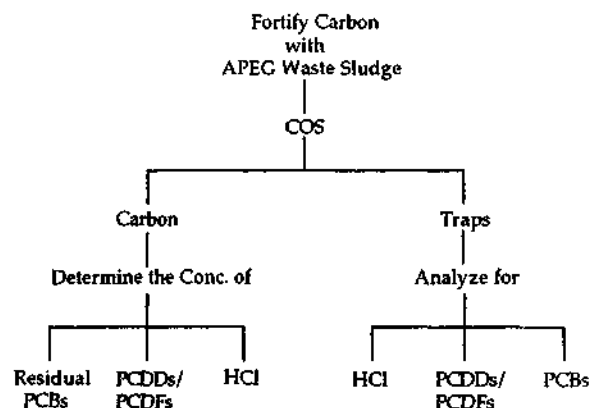


Figure 3. Flow Diagram of the Approach for Mass Balance.

of oxygen flow rates included by experimental scope. The condition was 250 mL/min oxygen flow. The upward velocity of flame front was approximately 3.70 cm/min at this condition. The velocity was calculated by dividing the height of carbon bed in the reactor tube by the total burn time.

Removal and Destruction Efficiency of PCBs. A mass balance approach was utilized for removal and destruction efficiency of PCBs in a quantitative manner. A flow diagram for this approach is shown in Figure 3. The approach is subjected to determination of removal and destruction efficiency by measurements of the initial and final PCBs and the ultimate mineralized product such as HCl. The possible oxygenated by-products, especially polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs); were also monitored.

Nearly all of the PCBs were destroyed at 1% waste loading rate. The removal and destruction efficiency was $\geq 99.99\%$. The efficiencies of 99.84% and 99.71% were also obtained even when contaminant loading is 5% and 10%, respectively. The efficiency at 20% loading rate was moderately lower with the value falling to 98.83%. At higher loading levels of $\geq 30\%$, flame front occurred inconsistently at times, resulting in considerably decreased efficiency (91.54%). The efficiencies for removal and destruction of PCBs in waste are shown in Figure 4. Only a small portion (5%-10%) of the carbon was consumed at 1%-30% waste loading ranges during the process, so the carbon is recyclable many times. All wastes were run in single COS cycle under optimum condition. Even if successive COS cycles are capable of complete disposal of PCBs, they will pay a price in cost-effectiveness related with carbon loss. The removal and destruction efficiency was also supported by the fact that almost all of the PCBs were accounted as chloride in the impinger traps. Furthermore, no PCDDs or PCDFs were found at GC-MS detection levels of ppb in the regenerated carbons or in the impinger traps. This is a significant discovery and bodes well for the process, since the conventional incineration of PCBs is beset with toxic polychlorinated compounds.

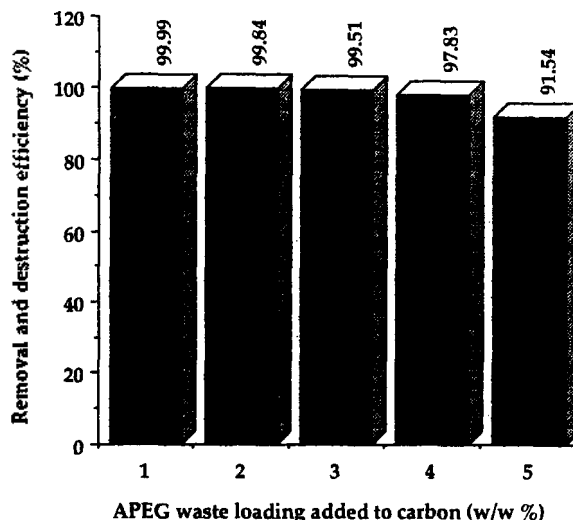


Figure 4. Effect of Waste Loading on Removal and Destruction Efficiency of PCBs.

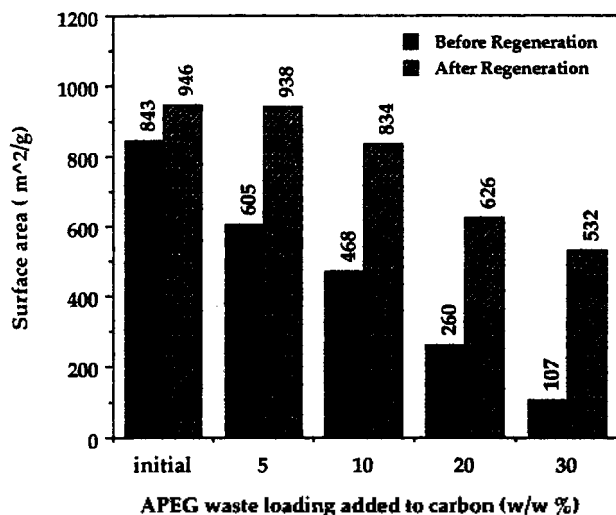


Figure 5. Effect of Waste Loading on Surface Area.

Evaluation of Carbon Surface Characteristic.

The surface area measurements for spent carbon before and after COS process are given in Figure 5. The surface area of the carbon was decreased with increasing amount of wastes. The adsorptive capacity of the spent carbon was largely restored after regeneration. The results clearly demonstrated that the COS is effective in destroying PCBs and, at the same time, recovering all of the original surface area.

Conclusion

A new thermal process, termed counterflow oxidative system (COS), has been developed and evaluated for its applicability in several environmental areas. The entire process is carried out with self-sustained flame front. The temperature of flame front is high enough, and suitable for disposal of organic compounds which resist thermal degradation. Optimization conditions were determined with varying parameters such as oxidant flow rate and waste/carbon ratio to balance removal and destruction efficiency for adsorbed organics and gradual carbon loss during COS process. It was observed that, under optimum condition, PCB removal and destruction efficiency in APEG waste was 99.99% or better while bulk of carbon $\geq 90\%$ was re-

covered. The process did not result in the formation of any toxic by-products such as PCDDs and PCDFs. The surface area of regenerated carbon was significantly recovered. Clearly, it is anticipated that a continuous process of this type would have far reaching consequences for management of growing hazardous waste problem.

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