

PCB DESTRUCTION PRACTICES AND TECHNOLOGIES IN THE U.S.

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ABSTRACT:

During the past decade, a plethora of processes have been developed for the destruction of polychlorinated biphenyls (PCBs), an environmental contaminant of increasing concern. A survey of some recent commercial and experimental methods, including thermal, chemical, and biological procedures, is presented here.

INTRODUCTION:

PCBs are omnipresent environmental contaminants. According to EPA estimates¹ from the late 1970's, the environmental release of PCBs amounted to some 441 million pounds, 34% of which consists of contaminated soil, water, sediment and air. It is probable that all residents of the United States have measurable levels in their bodies. The occurrence of PCBs in samples of fish and milk at levels of about 2000 ppm exemplifies the process by which Americans have achieved quantifiable concentrations in adipose tissue and blood. Because these materials are known to concentrate through the food chain, there has been much effort devoted during the past ten years to removing PCBs from decommissioned transformers, ground spills/leakages and sludges, and destroying these compounds by chemical, biological, thermal and other means.

THERMAL DESTRUCTION TECHNIQUES:

Thermal processes include those in which PCBs are either burned, pyrolyzed, catalytically oxidized at temperatures above 500°C, or reduced at molten metal bath temperatures. Detailed descriptions of various incineration processes are available². Multiple chamber and rotary kiln incinerators are the most versatile, being able to accept solid, slurry, liquid, sludge, fume and containerized wastes.

Chemical Waste Management operates two rotary kiln TSCA permitted incinerators in Chicago, Illinois and Port Arthur Texas, which accept PCB contaminated oils, sludges and solids, including capacitors and transformers. Secondary combustion chamber gases have a residence time of at least two seconds at a minimum temperature of 1205°C in these units. Greater than 99.9999% destruction of PCBs is invariably achieved. The Chicago incinerator burns between 100,000 to

110,000 gallons of PCB-contaminated liquids/week along with some 50,000 to 60,000 pounds of PCB solids. The Port Arthur facility has successfully completed a trial burn with a chlorine removal efficiency of 99.99%. A TSCA permit for this facility is anticipated for the last quarter of 1990. Port Arthur's permit will allow for the destruction of nearly 23 million pounds of PCB liquids, and over 367 million pounds of PCB solids per year, or about 150 times the quantity of solids currently being destroyed at the Chicago site.

Mobile and in situ thermal technologies have been proposed as potential solutions for cleanup of some Superfund sites³. Of 90 EPA records of decision (RODs) released between January 1987 and July 1988 and involving treatment methodologies, 15 recommended thermal treatment. An examination of 107 RODS issued for 97 Superfund sites between 7/1/82 and 9/30/89, revealed that 36 proposed some form of thermal treatment, with 28 specifically recommending incineration, for at least a portion of the remediation.

Another relatively new pyrolytic technique, which operates at even higher temperatures (>1500°C) involves the formation of a transfer plasma from a high voltage ac arc⁴. A small scale unit, capable of treating about 50 gallons of 1000 ppm PCB-contaminated oil/day is estimated to cost about \$50,000, with an operational cost of \$1.93/gallon, if co-fueled with product gases. The authors claim a destruction efficiency of >99.999%, but this is not supported by the data shown in their publication.

As reaction temperatures decrease, so do destruction efficiencies; thus other reactants or catalysts may have to be employed to insure thermal decomposition. At 580°C, decachlorobiphenyl (about 8300 ppm in an argon carrier), passed over magnesium, aluminum, α -alumina or magnesia with contact times of about eight seconds, was decomposed to >99.999%⁵. The principal products of this reaction are the metal chloride and carbonaceous char.

CHEMICAL DESTRUCTION OF PCBs:

The Franklin Institute APEG process⁶, which was the subject of a patent issued in 1982, involves reacting PCB-contaminated waste with either a mixture of an alkali metal, or metal hydroxide and a polyethylene glycol (usually PEG 400); or preforming the reagent (NaPEG or KPEG) and reacting it with the waste, generally at temperatures between 150°-250°C for periods of one to several hours. For more highly chlorinated PCBs, such as those present in aroclors 1260 and 1254, it is possible to achieve >99.9%, and probably even >99.99% destruction using this method. For electronic reasons, the lower PCB congeners are rather unreactive, requiring either much higher temperatures, or very extended reaction times. In all cases, however, only one, or possibly two of the chlorines on any given ring will react with this reagent. The lowest congeners probably do not react at all.

Joint studies were conducted by the U.S. Navy Civil Engineering Laboratory and the U.S. EPA's

Risk Reduction Engineering Laboratory, with PCB-contaminated soil on the island of Guam⁷. With initial soil concentrations averaging about 3500 ppm, a mean destruction efficiency of 99.84% was claimed, with no congener group exceeding 2 ppm in concentration.

A further refinement of the APEG process is Galson Remediation Corporation's dechlorination process, which utilizes KPEG and either sulfolane (tetrahydrothiophene-1,1-dioxide) or dimethyl sulfoxide as cosolvents⁸. These materials are estimated to provide a doubling, and quadrupling of KPEG reaction rates, respectively, as well as a concomitant increase in dehalogenative efficiency. Pilot studies at the Wide Beach Development site indicated that the reagent could be recycled effectively over a seven run series. This reagent system was also employed in the treatment (to <2ppm PCB) of 6,000 gallons of contaminated oil at the Niagara-Mohawk Power Corporation site in 1986. It was further utilized the same year in the decontamination (to <2ppm PCB) of 12 tons of PCB soil at Bengart-Memel. PCB processing costs (exclusive of mobilization/demobilization) are estimated at \$250-\$270/ton of contaminated soil.

Chemical Waste Management has also employed this technology (with the involvement of Galson) for the destruction of 6000 gallons of dioxin-contaminated oil sludge and diesel rinse at the Western Processing Superfund site in Kent, Washington. This work was completed over an eight week period during the summer of 1986, and dioxin concentrations of 120 ppb were reduced to <300 ppt.

General Electric has developed a process which utilizes an alkali metal derivative of a monomethylated polyethylene glycol⁹. At 140°C, >99.9% of the PCBs in a 500 ppm PCB-containing oil were destroyed within 45 minutes. Another General Electric patent¹⁰ utilizes alkali metal mercaptides in conjunction with PEG or a quaternary ammonium or phosphonium salt as a phase transfer agent, to effect the destruction of PCBs. At 75°-100°C and 1-24 hours, PCB destructions of >99.9% were obtained in some cases. However, large excesses of reagents and phase transfer agents were employed.

Chemical Waste Management, Inc. is developing a new procedure (KGME process) which uses the potassium derivative of 2-methoxyethanol for the destruction of PCBs¹¹. For aroclors 1254 and 1260, >99.99% destruction efficiencies have been achieved, at temperatures ranging from 90°-110°C, in as little as three hours time. Since stoichiometric, or even substoichiometric quantities of reagent are employed, and KGME has only about 25% of the molecular weight of KPEG, much less KGME is required, compared to KPEG. This results in a considerable savings in both the costs of reagents and ultimate disposal. A practical application of this technology will be demonstrated as part of a remediation of the Resolve, Inc. Superfund site (Massachusetts) during this fall.

Reduction reactions for PCB destruction usually involve the use of either a metal (e.g. sodium), hydrogen (either as the element, a metal hydride, H-radical, or other H-donor), or "solvated electrons" (sodium naphthalenide). The sodium (Acurex) process has been employed by Chemical Waste Management at its Model City, New York site. During a two month period in the summer of 1986, about 870 gallons of PCB-contaminated oil was treated with sodium metal. Initial PCB concentrations ranged from about 250 ppm for 380 gallons and about 1500 ppm for the remaining 490 gallons. In each case, PCB concentrations were reduced to <1 ppm, with some runs as low as 0.05 ppm.

The use of sodium has some drawbacks, however, including cost, potential hazards associated with its use, and the fact that it is most effective in treating relatively low PCB concentrations (although the Acurex process has treated up to 10% PCBs successfully). Some of these difficulties are overcome by converting sodium to sodium naphthalenide¹² (NaNp, General Electric process). This process has been commercialized by Goodyear Tire and Rubber Co. A cyclic lab-scale reactor for the removal of PCBs with NaNp has been described, in which 99.5% destruction is realized after 15-30 minutes of operation at ambient temperature¹³.

The ENSR (formerly Sunohio) PCBX process¹⁴ uses sodium and a proprietary replacement for naphthalene, which is a priority pollutant. This reaction produces polyphenylene, which precipitates from the reaction mixture. Oil processing costs are estimated to be \$4/gallon, with destruction efficiencies of >99.9% (1100 ppm initial concentration). Over 30,000 gallons of transformer oil were reclaimed by this process in 1981.

Hydride reagents for PCB treatment include lithium aluminum hydride, sodium borohydride and sodium hydride. LiAlH_4 and NaBH_4 have both been employed in analytical PCB determinations, as a means of quantitating PCBs by the determining the biphenyl formed from their reduction. The borohydride is used in the presence of Ni^{2+} , which gives rise to H_2 and Ni_2B^{15} , which ostensibly catalyzes the reduction. Sodium hydride in the presence of alkylamine, has been used to reduce PCB-contaminated oils (up to 20,000 ppm), giving 99.9% dehalogenation¹⁶.

An interesting low temperature hydrogenolysis of PCBs has been described¹⁷. Sodium hypophosphite is used as the H-donor, in the presence of 5% Pd/C. The reduction is carried out at 50°-90°C and ambient pressure for one hour. Destruction efficiencies exceeding 99.9% are obtainable by this method.

MODAR, Inc. has developed a supercritical fluid oxidation process¹⁸ which employs water in its supercritical state (above 647°K and 22.1 MPa). Under these conditions, oxygen and organics are solubilized in the supercritical medium, while inorganics have greatly reduced solubilities. In a pilot scale demonstration of the process, with an initial aroclor 1260 concentration of 1600 ppm, a destruction efficiency of 99.995% was achieved.

Low temperature oxidative removal of PCBs has not been attempted commercially, although the feasibility of such a method has been recently demonstrated¹⁹. Using ruthenium tetroxide, a mixture of aroclors 1242, 1254 and 1260 was converted to CO₂ and HCl, at temperatures ranging from 50° to 70°C. Ruthenium dioxide produced in the reaction is reoxidized with aqueous NaOCl. The reaction is believed to proceed through a free radical mechanism.

The USEPA has recently revealed new technology for PCB destruction²⁰, which it is attempting to commercialize. This base-catalyzed decomposition (BCD) process utilizes a proprietary hydrocarbon as a hydrogen source/solvent and a base catalyst, at temperatures from 250°-340°C, to dechlorinate PCB contaminated soils, sludges and oils. Radical dechlorination is suggested.

MISCELLANEOUS METHODS:

The superoxide radical anion has been generated electrochemically from air or oxygen dissolved in DMF at 1 atm. It is capable of converting PCBs (e.g. aroclor 1268) to carbonate and chloride anions²¹. In the absence of air, electroreduction occurs, yielding successively less chlorinated intermediates, and finally, biphenyl. Resource Engineering, Inc. has a small portable demonstration unit capable of electrochemically processing four gallons per hour of contaminated oil²².

A number of photochemical methods for PCB destruction are known, most of which involve the use of ultraviolet radiation to produce ozone. A unit capable of treating 40,000 gal/day of 50 ppm PCB feed to 1 ppm has been described²³. In the presence of sodium borohydride, photodehalogenation is enhanced²⁴, possibly through a radical chain propagation, electron transfer, direct attack by borohydride on the excited chloroaromatic, or a combination of these mechanisms.

PCB remediation through biological/biochemical methods has been of interest for some time, particularly in light of recent reports that PCB concentrations in highly contaminated Hudson River sludge samples are undergoing dehalogenation by anaerobic bacteria²⁵. These organisms appear to dechlorinate PCBs, while aerobic ones oxidatively convert these partially dechlorinated products to chlorobenzoic acids, possibly in concert with photochemical processes²⁶. General Electric is investigating two PCB-contaminated soil cleanup processes²⁷, one of which involves extraction with aqueous surfactants, while the other utilizes bacterial degradation with *Pseudomonas putida*. Both techniques look promising, but still require considerable development.

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