

Decontamination and Disposal of PCB Wastes

by L.E. Johnston*

Decontamination and disposal processes for PCB wastes are reviewed. Processes are classed as incineration, chemical reaction or decontamination. Incineration technologies are not limited to the rigorous high temperature but include those where innovations in use of oxidant, heat transfer and residue recycle are made. Chemical processes include the sodium processes, radiant energy processes and low temperature oxidations. Typical processing rates and associated costs are provided where possible.

Introduction

The decontamination of materials or equipment containing polychlorinated biphenyls (PCBs) and the disposal of the waste material generated are technological concerns that occupy a crucial place in the overall concern for the management of hazardous waste. The problem of PCB waste, although it is not a large problem, has been popularized and politicized out of proportion. Some of the fundamental characteristics of the PCB molecule that have heightened this concern are: persistence and therefore ubiquity, ease of detection, suspected carcinogenicity and contamination by, or precursor to, other toxics. These properties have led to unprecedented requirements for emission control and rigor in the processes designed for PCB waste disposal.

This has created problems in the preparation of an objective overview on the subject at least in the North American context. First, the disclosure of scientific information is often obtained first through the press release and much later through the scientific literature, if at all. This reflects the enormous political and financial importance attached to the solution to the central hazardous waste problem in society. It also puts a reviewer on the defensive because anything you say is open to criticism based on: failure to include this or that process, perceived bias should one process come out in a less favorable light in a comparative analysis and lack of the most up-to-date information in a rapidly developing field where information is not openly discussed for proprietary reasons and, where it is discussed, is featured by extravagant claims. As a result, this review is struc-

tured on the basis of types of waste disposal process and, where examples are given, they are exemplary only, not comprehensive. Waste disposal deals generally with the destruction of PCB in a complex waste mixture. Decontamination deals with the removal of PCB from a material you want to recover or cannot totally destroy. Of the usual list of destruction technologies available, only the more intense technologies are worth consideration. Thus, high temperature incineration, in one form or another, is the first waste disposal technology considered. The other principal technologies are those utilizing chemical reaction. This involves the application of strong chemicals (sodium, oxygen, chlorine) or intense radiant energy. Under decontamination, the sodium processes are listed again because of the special place transformer decontamination occupies in this field. Some adsorption processes have also been attempted for lightly contaminated oils, etc. The decontamination of equipment is done by a combination of extraction and distillation. Finally, some case histories will be offered for the decontamination of buildings, etc., contaminated with PCB through a fire situation.

Finally, by way of introduction, the following basis has been used in preparing this review. Only relatively fast, efficient technologies have been highlighted. Other, soft technologies, that are slow or inefficient like most biological processes have been omitted. Only processes with the potential to handle real wastes are discussed. Typically, the basis for cost and energy considerations has been a 20% solution or mixture of PCB in oil for the liquid waste and a 10% PCB content in solid waste that may also contain soil, metal paper, cloth or plastics. The experience is mainly North American, with the specific regulatory and cost basis being Canadian as prevailing in 1982.

*Dillon Consulting Engineers and Planners, Box 1850, Station A, Willowdale, Ontario, Canada M2N 6H5.

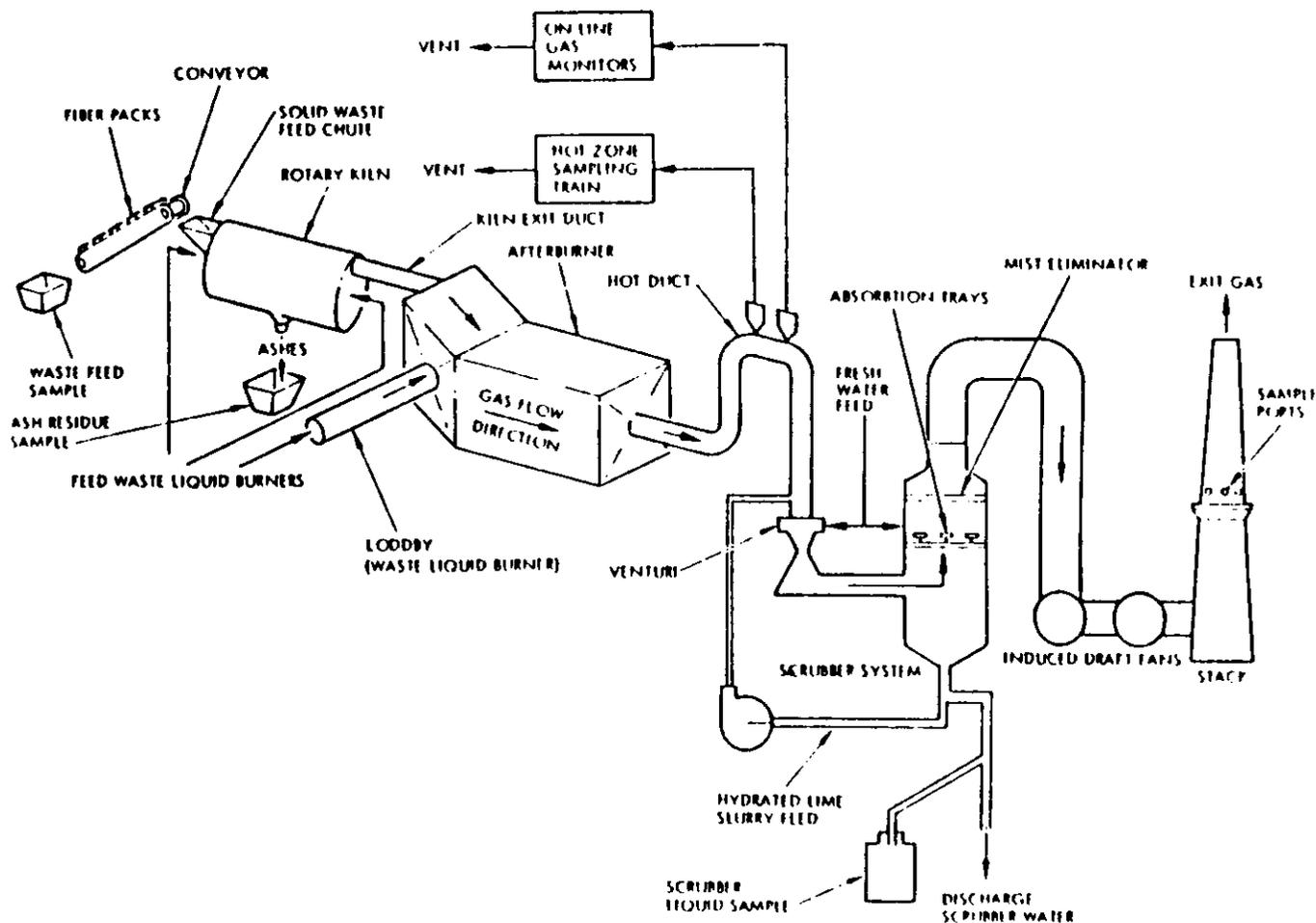


FIGURE 1. Schematic of Rollins incinerator.

Waste Disposal Incineration

The distinction made here between incineration and other chemical processes is artificial. Of course, an incineration process is a chemical process, but because the incinerator is designed primarily to control temperature and residence time, often through combustion of support fuel, the distinction is worthwhile. In the other (chemical) processes the reaction between PCB and the chemical reagent is more often the controlling feature.

Conventional Incineration. The incineration of PCB in Canada and the United States is regulated by a recipe for incineration conditions. These conditions were developed in a laboratory study on PCB destruction and suggest adequate destruction will only take place under the following minimum operating conditions: 2-sec residence time at 1200°C with 3% excess oxygen; 1.5 sec residence time at 1600°C with 2% excess oxygen. In the discussion that follows these criteria are often used to judge success, but, as we shall see, they are not always necessary to achieve adequate destruction.

Waste Incinerators. PCB waste disposal by incineration in a waste incinerator has been approved in a number of locations in the U.S. A typical operation is that of Rollins Environmental Services, who operate several waste incinerators of a similar design. The essential features of the Rollins design are given in Figure 1. Solid wastes in 0.2 m³ fiber drums are fed to a Loddby furnace (1.6 m diameter × 4.9 m long). Fuel and/or liquid wastes are atomized by compressed air and fed to the combustion chamber in a fashion that produces a rotating flame. Temperatures reach 1500°C in the combustion zone. An afterburner is provided (4m × 4.3 m × 10.6 m long) where temperatures are typically 1300°C. The residence time is 2 to 3 sec in the combustion chamber plus afterburning zone.

The combustion products are treated in a Venturi scrubber followed by an absorption tower. Lime is used to neutralize acidic components of the gas stream. Destruction efficiencies have been measured at 99.9999% for liquid PCB wastes and in excess of 99.999% for PCB in shredded capacitor waste.

This incinerator is able to process PCB waste very inexpensively because of the large throughput of other

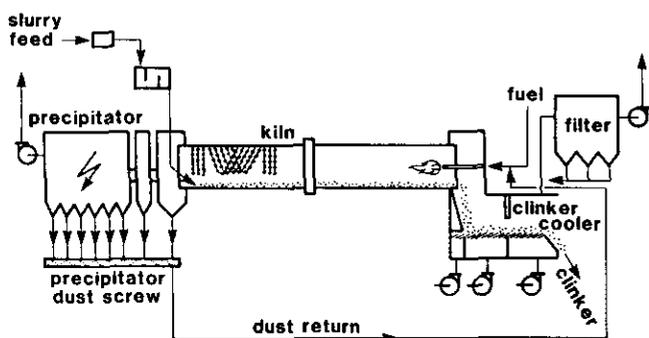


FIGURE 2. Wet process cement kiln.

wastes which permits the economies of scale. Based on a 300 day/year continuous operation at a feed rate of 2300 kg/hr, the cost of PCB destruction here amounts to about \$0.05/kg.

Other waste incinerators operating in the U.S. include the ENSCO incinerator in Arkansas and the SCA incinerator in Chicago. The ENSCO incinerator is noteworthy in that it is a converted steam plant in an abandoned oil refinery. It, along with the Rollins incinerator, led the way in the difficult early approval process for PCB incineration.

A number of private industries are also approved to destroy PCB in the U.S. although these are mainly limited to the destruction of their own wastes. These include: General Electric in Massachusetts and New York and Dow Chemical at several sites. The Dow incinerators tend to be dedicated chemical waste incinerators, somewhat smaller, more specialized and therefore more costly to operate.

Cotreatment Incinerators. A number of industrial processes that make use of high temperature combustion are suited to destroying PCB in the high temperature zone of the process. The principal example of such a cotreatment is a cement kiln.

St. Lawrence Cement Co. operates a wet process kiln just west of Toronto (Fig. 2). The calcining reactions take place in a rotary kiln, 3.5 m in diameter by 123 m long. In a test incineration, PCBs were fed along with the heavy fuel oil. The incineration of PCB in the kiln was part of a program to utilize waste chlorinated hydrocarbons to replace part of the fuel requirements and part of the chlorine requirement needed to produce low alkali cement (Na and K are volatilized as chlorides). The conditions in the kiln are ideal for PCB destruction: temperatures up to 2100°C and residence times of the order to 30 sec. Destruction efficiencies at St. Lawrence were at least 99.99% but local political pressure prevented approval of this process.

Not shown in Figure 2 is the pretreatment adjuncts to this process. To handle solid wastes, a shredder would be necessary. With this sort of added equipment and based on a treatment rate of about 700 kg/hr of liquid wastes or 350 kg/hr of solid wastes (900 Mg/day of cement production) the cost of PCB destruction is esti-

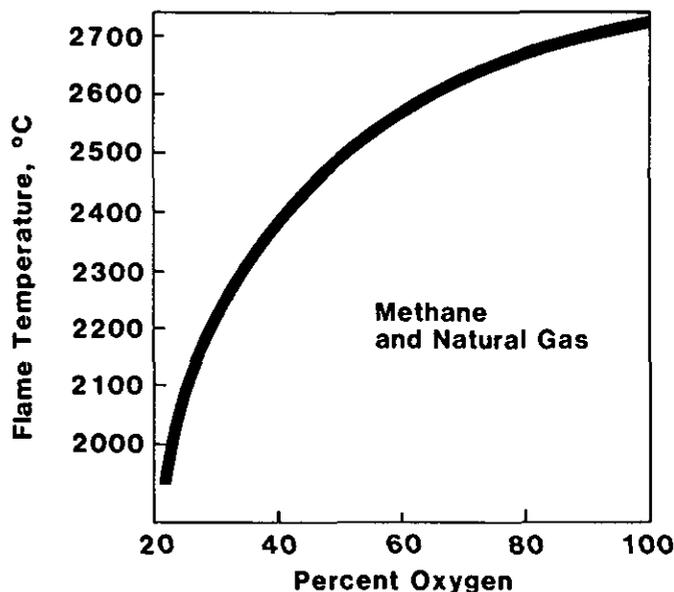


FIGURE 3. Pyro-Magnetics mobile hazardous waste processor.

ated to be \$0.14/kg. The treatment of solid waste is, however, a concern for the cement kilns, since the metal oxides produced typically from iron and steel will adversely affect the quality of the cement.

Other cotreatment examples include other kilns like lime kilns, on which some tests have been done and an alumium melting furnace belonging to Alcoa in Iowa. The burning of contaminated oil in power boilers at oil and coal-fired electricity generating stations has been demonstrated and approved at a number of locations in the U.S. In power boilers only the larger units approach the recipe conditions for PCB destruction. As a result, regulations and guidelines restrict the PCB concentration in waste oils to about 500 mg/kg. However, there is no reason to suggest that with adequate verification this co-treatment process could not be more widely used. In fact, power generation utilities often are major holders of PCB inventory and as such have a responsibility to manage their own wastes.

Nonconventional Incinerators. There are a variety of techniques that can be used to achieve the same results as conventional incineration where a hydrocarbon is burned in air under optimum conditions of space and time. These techniques include: enriching the combustion air with oxygen, increasing the oxygen concentration above that achievable in air, increasing the rate of heat transfer to the waste molecules, using catalysts or accepting lower efficiency in favor of high destruction rate with a recycle of residue. Each of these techniques or combinations thereof are exemplified by a destruction process below.

Oxygen Incinerators. The gain in temperature by use of higher concentrations of oxygen is illustrated in Figure 3. Using natural gas or methane, the flame temperature achievable can be increased from 2000°C in air

MOBILE HAZARDOUS WASTE PROCESSOR

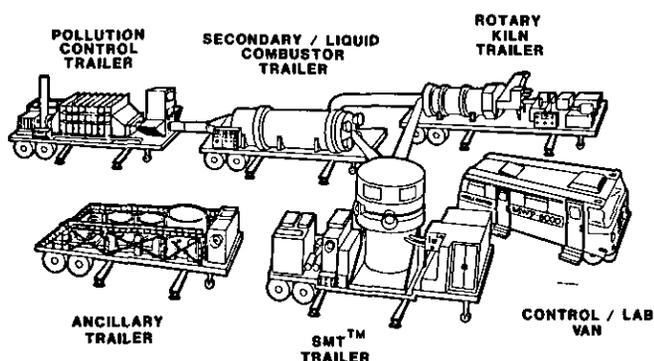


FIGURE 4. Variation of flame temperature with oxygen concentration.

to 2700°C in pure oxygen. The processing advantages are embodied in the PyroMagnetics integrated waste destructor illustrated in Figure 4. The oxygen incinerator is 0.8 m in diameter by 2.4 m long and receives directly injected liquid wastes. The combustor is followed by a burnout zone of the same cross section, 10.7 m long. Temperatures achieved are of the order of 2200°C with a 2-sec residence time, well in excess of the recipe conditions.

This unit has a further technological innovation, the Special Melting Treatment Unit (SMT), which makes use of an inductively heated bath of molten iron into which solid wastes can be fed. In the iron bath the solids are melted and the PCBs volatilized and/or pyrolyzed. The off gas from this melting unit is ducted into the oxygen incinerator. The Pyro-Magnetics unit also includes a rotary kiln unit, gas scrubbing unit and a mobile laboratory.

This unit can be fed 2700 kg/hr of solid waste or 0.6 m³/hr of PCB liquid waste at a 50% concentration in fuel oil. The overall cost of operating this process is estimated at \$0.24/kg with the perceived advantage that the unit is mobile. Destruction efficiencies in excess of 99.9999% have been demonstrated.

ENSCO, the waste incinerators mentioned above have recently reported the development of an oxygen-enriched-air incinerator. They have successfully destroyed PCBs using 50% enriched air stream achieving temperatures of the order of 2200°C. Their configuration appears to be similar to that of Pyro-Magnetics.

Molten Salt Incinerators. The advantages of higher oxygen content per unit volume and a higher rate of heat transfer can be illustrated by the molten salt destruction process. Rockwell International has pilot-tested units that cause the PCB oxidation to take place in a molten salt medium, mixed sodium carbonate and sodium chloride. Both the oxidant and the PCB molecule can be dissolved at higher concentrations in this medium than in air mixtures like those found in a conventional incinerator.

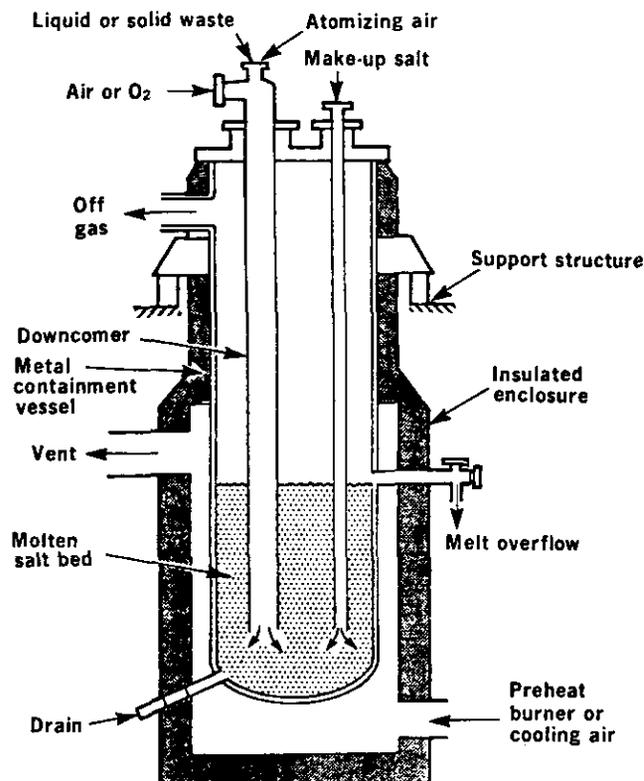


FIGURE 5. Rockwell molten salt incinerator.

The physical arrangement Rockwell used is given in Figure 5. Typically the reactor is 0.85 m internal diameter by 4 m high. It contains 1100 kg of salt (0.9 m deep when quiet) which is fed as a carbonate but is converted to a chloride as the product HCl is absorbed. This simplifies the gas scrubbing ancillary to the process. Effective operation persists up to <2% sodium carbonate and 20% ash content in the melt.

Typical pilot runs covered the temperature range 800 to 1000°C with a residence time of 0.25 to 0.5 sec. Oxygen was fed at over 100% stoichiometric excess. Destruction efficiencies exceeded 99.9999%, so that it is apparent these are significantly milder conditions which are still able to achieve acceptable destruction efficiencies because of the oxidant concentration and the high rate of heat transfer.

Processing rates were up to 100 kg/hr of waste. The process is capable of handling liquids and solids. Support fuel is only required if the waste contains less than 10,000 kJ/kg. The estimated cost of destruction is \$1.52/kg of PCB. This relatively high cost is attributed to the cost of sodium carbonate and support fuel.

Fluid Bed Incinerators. Another division of Rockwell has been evaluating fluid bed combustion of PCB. In this case advantage is taken of higher heat transfer rates in a fluid bed and the potential to be able to use a catalyst in the system. The Rockwell fluid bed system is illustrated in Figure 6. The fluid bed is composed initially of sodium carbonate and converts gradually to

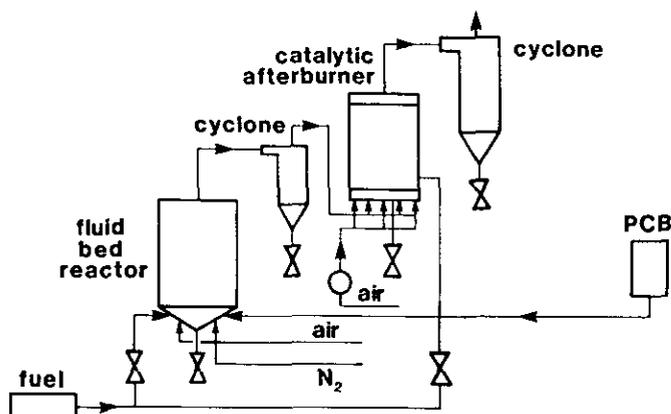


FIGURE 6. Rockwell fluidized bed incinerator.

sodium chloride as the HCl is absorbed. A chromium(III) oxide supported on alumina is used as the catalyst. Operating temperatures in the two beds are 600°C and 700°C, respectively. Destruction efficiencies in excess of 99.9999% have been observed.

As stated this is a pilot unit upon which scale-up data was collected. It is estimated that a full-scale unit processing 4500 L/day of liquid waste would process PCB for about \$1.30/kg.

Diesel Processes. The final example of nonconventional incineration is PCB destruction in a diesel engine. This concept takes advantage of the high processing rate in a small, portable unit with the capture for recycle of PCB not destroyed on the initial passage through the unit.

The process makes use of a conventional diesel engine with exhaust gases scrubbed and passed through activated carbon. Destruction efficiencies of the order of 99.8% have been demonstrated. The residuals trapped on the carbon are presumably recycled by washing the carbon periodically with a suitable solvent.

The processing rate for PCB liquid wastes is 190 L/hr, with up to 75% PCB in the fuel. The unit of course would not be able to handle solids although the developers of this process in Canada, D&D Group have proposed an integrated facility in which PCBs are extracted from solid wastes, concentrated by distillation and destroyed in the diesel. Processing costs are estimated to be \$0.89/kg.

Chemical Processes

The chemical processes that have demonstrated successful PCB destruction are: sodium processes, radiant energy methods and low temperature oxidations. The sodium processes are generally applied to contaminated oil and can be considered decontamination processes. They are described here because PCB destruction takes place. Radiant energy processes involve either activation of the PCB molecule to the point where it decom-

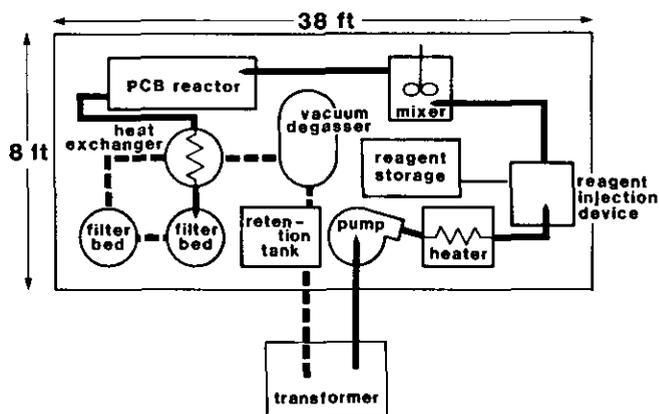


FIGURE 7. PCBX process.

poses or activation of a reagent molecule to facilitate its reaction with PCB. Low-temperature oxidations involve reaction with oxygen but not in the combustion mode that is found in an incinerator.

Sodium Processes. Sodium processes all rely on the same basic overall reaction. Sodium, in one form or another reacts with the chlorine on the PCB molecule, producing sodium chloride and an aromatic polymer based on the original biphenyl skeleton. There are three variations of this reaction: direct reaction with the sodium metal, preparation of a "sodium reagent" based on producing reactive ionic sodium stabilized by a highly aromatic carbanion which is then reacted with PCB and preparation of a sodium alcoholate which is then reacted with PCB.

The direct sodium reactions are being developed primarily by two utilities in Canada, Ontario Hydro and British Columbia Hydro. Their processes depend on dispersion of sodium in oil by mechanical means at temperatures above 100°C. The dispersed sodium is reacted with PCB in contaminated oil.

The second type of sodium process is typified by the production of a sodium reagent, like sodium naphthalide. The reaction sequence is as follows. A sodium sand is produced by dispersing sodium in mineral oil at 150 to 170°C. The mixture is cooled, and naphthalene dissolved in tetrahydrofuran is added, forming the sodium naphthalide. The reaction with PCB involves the addition of the naphthalide ion to the PCB molecule with the subsequent elimination of sodium chloride. A polymeric material and sodium chloride are produced and are removed leaving decontaminated oil.

A typical commercial development is illustrated by the PCBX process (Fig. 7). The continuous process is housed in a portable trailer and is capable of handling 2.3 m³/hr of contaminated oil. The contaminated oil is passed through the process in multiple passes. Contamination is typically reduced from thousands of milligrams/kg to less than 2 mg/kg. Costs of treatment are in the range of \$3 to \$4/kg of contained PCB governed mainly by the cost of the sodium reagent.

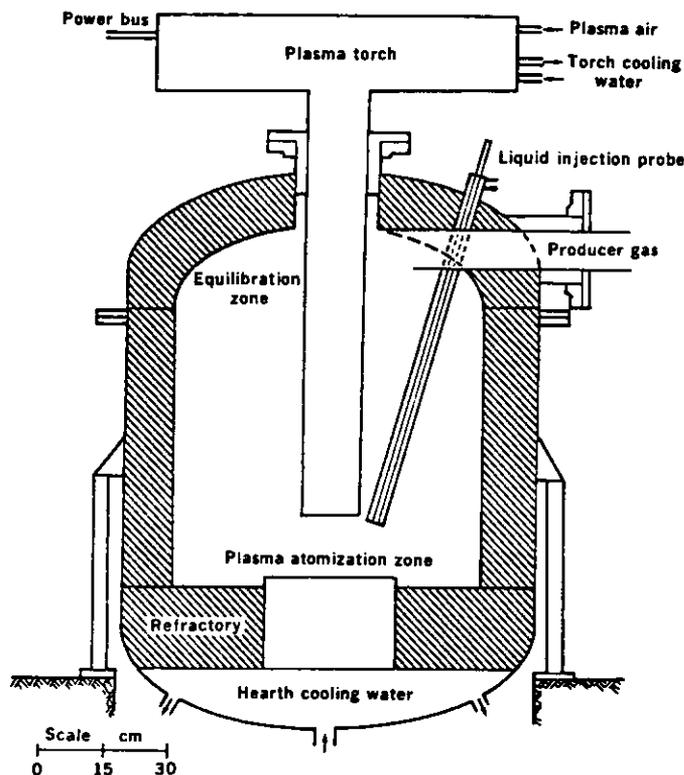


FIGURE 8. Plasma arc process.

A number of variations on the "sodium reagent" process make use of substitutes for naphthalene and THF, but all rely on the same basic reactions. The reagents are all sensitive to air, moisture, oil additives (antioxidants) and oil degradation products (alcohols and acids). Most processes involve some sort of pretreatment before PCB destruction.

The third sodium process makes use of a sodium alcoholate. The principal innovator in this field is the Franklin Institute of Philadelphia. Their reagent is called NaPEG. They react polyethylene glycol (typically MW = 400) with sodium to form sodium polyethylene glycolate, NaPEG. This reagent is much less sensitive to air and moisture and can be produced and shipped to the user. The NaPEG can be used to decontaminate oil or PCB in other wastes like contaminated soils. Costs are estimated to be similar to those for the naphthalide type reagents.

Radiant Energy Methods. Three methods based on the absorption of radiant energy have been chosen to illustrate this type of waste destruction technology. The three depend on radiation in the ultraviolet, infrared and microwave regions.

PLASMA ARC PYROLYSIS. The plasma arc process is based on the formation of a plasma by the passage of an intense electrical discharge through a collimated vortex of low pressure gas (Fig. 8). As the excited gas atoms relax, they transfer energy to the waste introduced into the reactor either by ultraviolet radiation or by direct contact with the waste molecule. In this way

the molecules are pyrolyzed, producing effluent gases of low molecular weight like carbon monoxide, carbon dioxide, hydrogen chloride, water and hydrogen.

The principal innovation in this technology is the plasma torch itself. Through a proprietary arrangement of gas flow, a collimated column of plasma can be struck between the torch acting as one discharge electrode and the hearth which acts as the other electrode. Typical electrical requirements are 1000 V d.c. at 300 amp, producing plasma temperatures of 50,000°K. The reactor is typically 1 m in diameter by 1.5 m high. Feed rates in the range 10 to 100 kg/hr are possible, with power requirements of 0.35 kW-hr/kg of waste.

Destruction efficiencies for PCB have been demonstrated in excess of 99.9999%. The overall heat balance is controlled so that the reactor outlet gases are typically in the range of 700°C. The plasma-forming gas can be any gas, so that the formation of toxics like dioxins can be minimized by excluding oxygen. Overall gas flow rates are very low, usually only a few percent of that required for the corresponding combustion. PCB destruction costs are estimated to be \$0.26/kg PCB. Liquid and solid waste can be handled in this reactor.

THAGARD HIGH TEMPERATURE FLUID WALL REACTOR. An interesting example of an innovative high technology process is the Thagard reactor, illustrated in Figure 9. The reactor features six radially disposed carbon rods that are electrically heated to the point they emit infrared radiation. This radiation is focused on an infrared-transparent central tube down which waste is passed. The waste is pyrolyzed by absorbing the IR radiation; if necessary, an absorption aid like carbon is added to the waste to enhance IR absorption.

The central tube is protected from the heated waste by the passage of an inert gas through its porous walls. The inert gas then flows like a fluid down the inside wall of the tube. Waste pyrolysis gases like hydrogen chloride, carbon monoxide, carbon dioxide, methane, water and hydrogen pass out of the tube with the inert cooling gas. The reactor is typically 30 cm in diameter by 9 m long. While it is in the early stages of development, waste treatment rates of about 150 Mg/day are projected. It will of course be able to handle both solid and liquid wastes. No treatment costs are estimated at this point in its development.

Microwave Processes. Two microwave processes have been studied in a preliminary fashion. The first is a microwave process that was being developed by Lockheed Aircraft until funding was withdrawn. This process depended on the activation of low pressure oxygen (0.1 atm) with microwave energy. The activated oxygen was then contacted with waste material in the gas phase resulting in efficient oxidation to carbon dioxide, hydrogen chloride and water in the case of PCB. The process had limited application because it dealt only with liquid wastes that could be readily volatilized.

A second process which is at present a laboratory process but has the potential for low temperature PCB destruction. Here, microwave pulses (>2 kW for <1

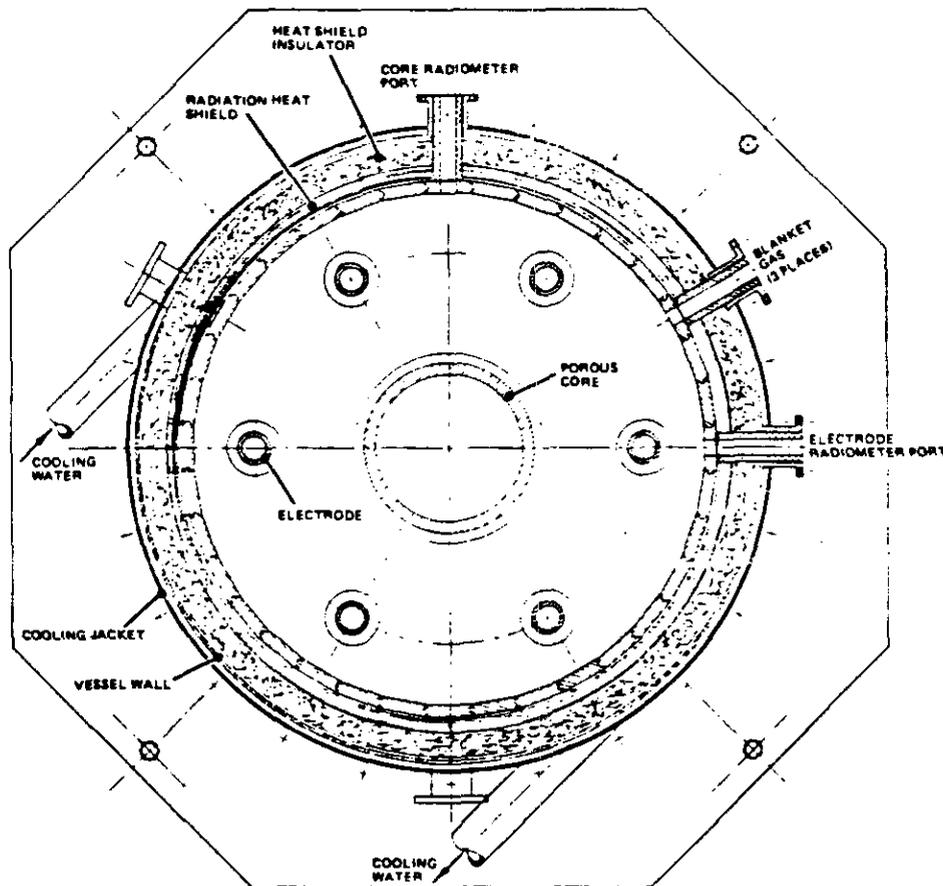


FIGURE 9. Thagard high temperature fluid wall reactor: horizontal section.

sec) are focused on a metal surface onto which oxygen has been absorbed. The oxygen on the metal surface is activated and reacts with the PCB molecule destroying it. A 10–15 sec pause between pulses keeps the temperature rise to only 10–15°C above ambient. The metal surface is in the form of a fluid bed of powdered metal fluidized in a recirculating flow of oxygen at 2 atm.

Low Temperature Oxidations

The oxidation of PCB at low temperatures has been demonstrated with oxygen and chlorine. The designation “low temperature” is relative to the high temperatures described for the incineration processes. Two processes are described here where the oxidation takes place at 400–600°C. Another process, wet air oxidation, has been tested in the 200–300°C range, but it has been found to be quite incomplete and requires very long residence times.

Supercritical Water Process. Modar Inc. of Massachusetts have developed a process that destroys waste in an aqueous medium at 400°C using air or oxygen at a total pressure in excess of the critical pressure of water, 250 atm. The process arrangement is shown in Figure 10. The wastes are slurried in water and pumped to the reactor. At the temperatures involved, water

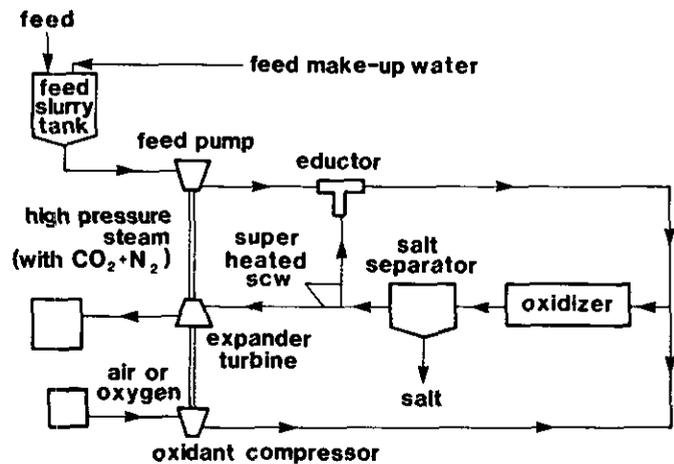


FIGURE 10. Modar supercritical water process.

becomes more like an organic solvent, totally dissolving the PCB and precipitating inorganic salts. This set of circumstances promotes the reaction. In the process the energy generated in the reaction by the oxidation is used to drive a turbine connected to feed pumps and air compressors. Reaction times are of the order of 2.5 to 4.5 sec and destruction efficiencies of the order of 99.99%. The process is being piloted during its development stage

in a 200 L/day reactor. Based on a 20× scale-up, the cost of PCB destruction with this process would be of the order of \$1.00/kg. In its present state of development the process would be limited to liquid wastes.

Chlorinolysis. Hoechst A.G. has made use of waste hydrocarbons as a feed stock for the production of carbon tetrachloride and by-product hydrogen chloride. In general, aliphatic wastes are preferred although aromatics such as PCB are accepted in the feed stock at concentrations of up to 5%.

Reaction conditions are in the range of 250 atm at temperatures of up to 600°C. The product carbon tetrachloride is separated by distillation so that high destruction efficiencies are not required as the still bottoms can be recycled.

Decontamination

Decontamination processes have been developed most extensively for transformers. The type of decontamination process applied depends generally on whether the transformer is a mineral oil transformer mildly contaminated with PCB or an askarel transformer which is to be retrofilled with a nonaskarel fluid. The mildly contaminated mineral oil transformer is usually handled with one of the sodium naphthalide type systems described above. These processes have been developed and applied by a number of companies in the U.S. Two of the main developers have been Sunohio (the PCBX Process) and PPM Inc. of Kansas City. The latter company has joined with the D&D Group to market their process in Canada. Decontamination from at least 10,000 mg/kg PCB to levels in the mg/kg range have been demonstrated.

Retrofilling askarel transformers with a nonaskarel fluid involves draining and flushing the transformer with a solvent. Upon retrofilling with the nonaskarel fluid, residual PCB content of the innards of the transformer leaches out to contaminate the new oil. This contamination has been reduced by circulating the filling fluid through an adsorption/absorption bed medium like neoprene for hydrocarbon oils and activated carbon for silicone oils. Processes are very slow, taking the order of months to act effectively. The beds are usually installed in cartridge form and can be attached to an operating transformer. In this case the decontamination takes place slowly but is effective in the long run.

Decontamination of transformers and capacitors that are destined for scraping or recycling of the metal values is often accomplished by extraction and distillation. A number of systems have been developed, most depend-

ing on washing the contaminated material (whole transformer or shredded capacitor) with clean solvent. The resulting contaminated solvent is decontaminated by distillation. The mechanical configuration takes a number of forms such as: countercurrent extraction, vapor-phase degreasing and Soxhlet extraction. Solvents used range from fuel oil and kerosene (where waste incineration is to be used for final disposal) to aliphatic chlorinated solvents and trichlorobenzene. In the case of trichlorobenzene advantage is taken of the fact that it is usually found in commercial mixtures containing PCB.

Other examples of extraction include vacuum distillation of PCB-contaminated hydraulic oils, where the hydraulic oil is higher-boiling than PCB, and liquid/liquid extraction where partitioning of PCB into different immiscible solvents takes place in much the same way as the analyst separates PCB from a sample substrate.

Recently, a novel technology has been demonstrated that involves extraction of PCB from solid wastes using critical point solvent extraction. Critical Fluids Systems of Massachusetts makes use of carbon dioxide at its critical temperature and pressure (24°C and ca. 75 atm) to extract PCB from solid waste. By decompressing the collected fluid, carbon dioxide is flashed off and recovered for reuse and PCB is collected as a liquid. The process has the advantage of not contaminating the waste substrate with solvent and it can be applied at low temperatures so that things like resin absorption systems and activated carbon are not degraded by heat treatments.

Finally, a number of fire incidents have been reported that required clean-up of a building contaminated by PCB and their toxic combustion products. The fire incidents and the clean-up procedures used are: Toronto, fuel oil and detergent washing; University of Manitoba, solvent washed (varsol); Binghamton, NY; vacuum cleaned, detergent washed and rinsed with organic solvents; Stockholm vacuum cleaned plus solvent washed; Skvode (Sweden), as above; Surahammar (Sweden), vacuumed, detergent-washed. This experience teaches that detergent washing in combination with solvent washing and vacuuming to collect the dust and soot seems to be an effective method of clean-up. Quick action is indicated to prevent PCB soaking into building surfaces made of polymeric organic compounds (paints and plastics).

The collection of much of the data reported in this review was done under contract to the Department of the Environment of the Canadian Government. Environment Canada has recently published the full detailed findings of our review and that report can be obtained from Ottawa.