Gas-phase chemical reduction of hexachlorobenzene and other chlorinated compounds: Waste treatment experience and applications

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Abstract

The industrial advances of the 20th century, and particularly those in the last half of the century, have created a legacy of hazardous waste stockpiles and contaminated sites. While significant progress has been made towards the execution of hazardous waste inventories and the reduction of hazardous waste generation, vast amounts of hazardous wastes still await treatment and disposal, including those contaminated by a wide variety of chlorinated compounds. Economical and effective methods are needed for the destruction of chlorinated organic wastes such as HCB, dioxin, PCBs and pesticides. Of particular importance is the provision of a technology that can be applied across the wide range of heterogeneous waste matrices and concentrations that typify hazardous waste stockpiles, from bulk solid material, to soils and sediments, to high-strength organic liquids.

Gas-Phase Chemical Reduction™ (GPCR™) is a non-incineration, hazardous organic waste treatment technology developed, patented and implemented by Eco Logic of Rockwood, Ontario. Internationally accepted and tested, GPCR has been used to treat HCB, PCBs, dioxins and furans, pesticides and other persistent organic pollutants.

In 1999, engineering trials were conducted on approximately 7 tonnes of HCB waste at Eco Logic's full-scale GPCR plant in Kwinana, Western Australia. The waste was produced as a by-product during the manufacture of chlorinated solvents, and was approximately 85 percent pure HCB. Results of the trials indicated that the system can effectively volatilise approximately 98 percent of the mass of the waste input to the TRBP (Thermal Reduction Batch Processor). Pre- and post-test analysis of TRBP solids indicated that at least 99.9999 percent of the HCB and chlorobenzenes present in the input waste were volatilised for destruction in the reactor. Reactor destruction efficiency measurements indicated at least 99.9999 percent destruction of HCB and total chlorobenzenes. Results of HCB testing, coupled with extensive hazardous waste treatment operations undertaken in the past 5 years, validate the ability of Eco Logic's GPCR process to treat HCB and other high-strength organic material for the commercial market.

Background

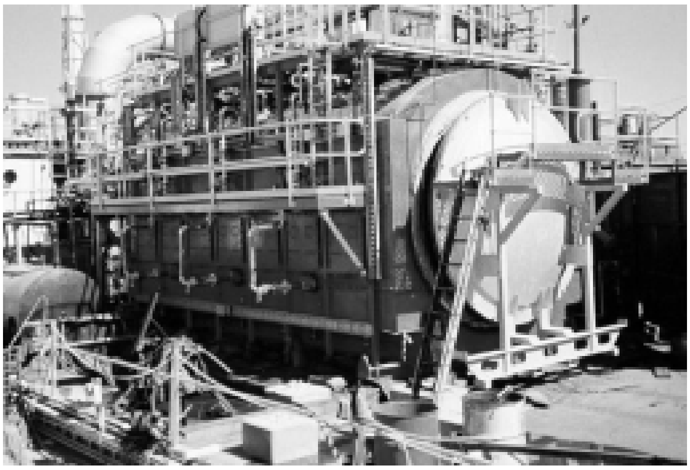
The industrial advances of the 20th century, and particularly those in the last half of the century, have created a legacy of hazardous wastes in and around industrial areas and harbours where many heavy industries were located. In recent years, significant progress has been made towards the execution of hazardous waste inventories and towards reducing the creation of new hazardous wastes. However, vast amounts of hazardous wastes still await treatment and disposal, including those contaminated by a wide variety of chlorinated compounds. Of particular concern is a group of chemicals termed "Persistent Organic Pollutants" (POPs), which include polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), dioxins and furans, and several other organochlorine pesticides. These compounds persist in the environment and can bioaccumulate, causing a variety of adverse health effects[1].

HCB in particular has received much attention in recent years. HCB is a chlorinated hydrocarbon that was used as a pesticide until 1958 and in the production of rubber, aluminum, dyes and wood preservative products. HCB is also created as a by-product during the manufacture of chlorinated solvents and other chlorinated compounds such as hydrochloric acid. Management of HCB stockpiles and new sources has been given special attention by Environment Canada and the United States Environmental Protection Agency[2], the United Nations Environment Programme[1], Environment Australia[3], and other organisations worldwide. While the total amount of HCB waste stockpiled worldwide is unknown, Eco Logic is aware of inventories in four countries that total in excess of 53,000 tonnes of drummed HCB waste and 550,000 tonnes of HCB-contaminated soil. In addition to the "legacy" problem of stockpiles of HCB and other POPs, these chemicals are still being created during various chemical and industrial processes[1,2].

Economical and effective methods are needed for the destruction of hazardous organic wastes including HCB. Of particular importance is the provision of a technology that can be applied across the wide range of heterogeneous waste matrices and concentrations that typify hazardous waste stockpiles, from bulk solid material, to soils and sediments, to high-strength organic liquids. In addition, a technology that can be used as a tool in pollution prevention will help to avoid the creation of additional stockpiles of hazardous organic wastes. Of primary importance is a technology that can treat such wastes, both legacy and newly-created, in a manner that is acceptable to the public and other stakeholders.

Gas-Phase Chemical Reduction (GPCR) is a non-incineration, hazardous organic waste treatment technology developed, patented and implemented by Eco Logic of Rockwood, Ontario. Internationally accepted and tested, GPCR has been used to treat HCB, PCBs, dioxins and furans, pesticides and other persistent organic pollutants. The process involves the gas-phase chemical reduction of organic compounds by hydrogen at temperatures of 850°C or greater. Organic compounds are ultimately reduced to methane, hydrogen chloride (if the waste is chlorinated), and minor amounts of low molecular weight hydrocarbons (benzene and ethylene). The hydrochloric acid is neutralised by addition of caustic soda during initial cooling of the process gas. The ability of GPCR to destroy organic contaminants with efficiencies in excess of 99.9999% has been proven numerous times in demonstration tests and commercial-scale operations. Suitable waste matrices include liquids, high-strength oils and solid materials. More information on GPCR chemistry, operation and experience can be found in Eco Logic's paper submitted to the 5th International HCH and Pesticides Forum in 1998[4].

In March of 1999, Eco Logic was contracted to conduct a commercial-scale engineering trial on HCB for a large waste-owner in Australia, at the full-scale GPCR plant located in Kwinana, Western Australia. The intent of the trial was to verify the ability of the GPCR process to effectively treat representative samples of HCB waste at full-scale and to determine major engineering parameters affecting adaptation of the Australian GPCR plant (which was originally intended for primarily PCB treatment) to a dedicated HCB configuration.



Thermal Reduction Batch Processor (TRBP) at the Kwinana, Western Australia Plant.
Liquid and solid wastes are placed into the TRBP, which is then heated to approximately 600°C in a hydrogen-rich (oxygen deficient) atmosphere. Contaminants that volatilise off of the solids and liquids are then swept into the GPCR reactor for destruction.The throughput capacity of the TRBP is approximately 75 tonnes per month; a single GPCR reactor and scrubber system can be equipped with two TRBPs, thus doubling the effective throughput capacity to about 150 tonnes per month.

Commercial-scale treatment of hexachlorobenzene

Description of waste processing facility and equipment

In May 1995, Eco Logic commenced operation of its first prototype full-scale GPCR plant at Kwinana, Western Australia. This plant is licensed to treat organochlorine compounds, and to date has treated in excess of 2,500 tonnes of waste including PCBs, DDT and other POPs.

The Kwinana plant is equipped with a single TRBP for treating bulk solid material and liquids, and a full-scale reactor/scrubbing system. A block flow schematic of the waste processing system is provided in Figure 1. Waste is placed in the TRBP, which is sealed and heated in an oxygen-free atmosphere to approximately 600°C. The contaminants that volatilise off of the waste are swept into the GPCR reactor, which operates at about 875°C; while some reduction of the organic compounds will occur in the TRBP, complete reduction occurs in the GPCR reactor. Gas leaving the reactor is scrubbed to remove particulate and acid, and then stored for reuse as a fuel.

Eco Logic's Full-Scale GPCR Reactor and Scrubbing System in Kwinana, Western Australia
Volatilised contaminants from the TRBP are swept into the reactor, where they are subjected to gas-phase chemical reduction in a hydrogen-rich (oxygen deficient) atmosphere at approximately 875°C. Gases exiting the reactor (primarily methane, hydrogen and hydrogen chloride) are scrubbed to remove heat, particulate and acid, and then stored for reuse as a fuel.

The facility at Kwinana operates 24 hours a day, 7 days a week, processing a variety of waste types and matrices, including PCB oil, PCB-contaminated bulk solids and organochlorine pesticides (OCPs). The majority of the material treated at the Kwinana facility is PCB-contaminated electrical equipment such as ballasts, capacitors and PCB oil. The facility has also processed a large quantity of OCPs (including DDT residuals) for various state authorities. The current throughput capacity is 70 to 75 tonnes per month (using a single TRBP - an additional

TRBP could be added to double the throughput capacity). Continuous improvements of TRBP operations have raised expectations of enhanced performance for a single TRBP of up to 90 tonnes per month. An added advantage is that the system can process different waste streams, such as liquids and solids, simultaneously.

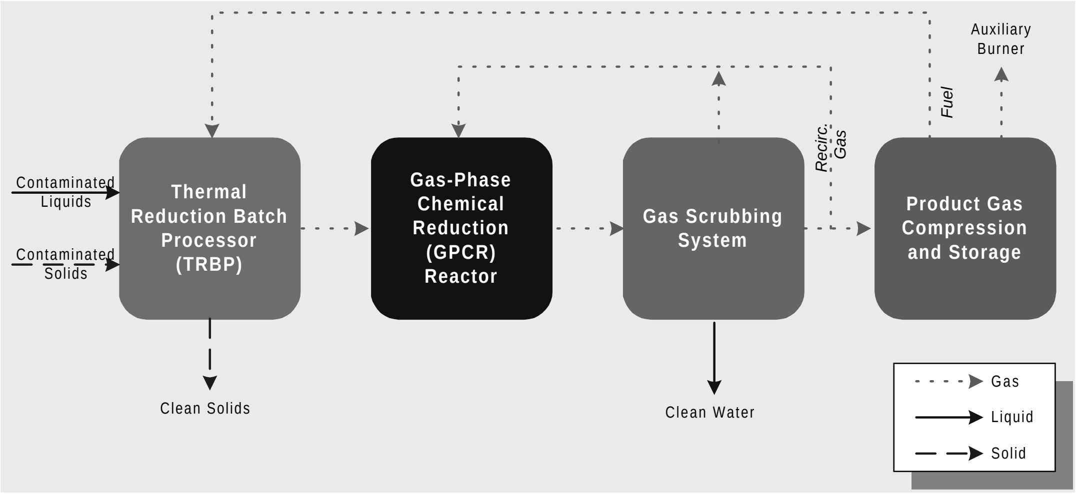


Figure 1. Waste processing block schematic

Overview of testing program

The engineering trials were comprised of three test runs of increasing waste input quantities (3, 9 and 27 drums for Tests 1 through 3, respectively). Throughout the trials, continuous monitoring of system operating conditions, and product gas composition occurred. Samples were taken of the input HCB waste and treated solids, scrubbing system samples (aqueous and particulate), and gases (product gas, ambient air and stack gas). These samples were analysed for a range of contaminants, including chlorobenzenes and volatile organic compounds (VOCs).

Hexachlorobenzene waste characteristics

HCB is a white crystalline solid with very low water solubility. The molecular formula of HCB is C_6Cl_6. The HCB treated during the trials was created as a by-product during the manufacture of chlorinated solvents. Some physical and chemical properties of HCB are provided in Table 1.

Table 1. Physical and chemical properties of HCB

Description	Units
Molecular weight	284.79 g/mole
Vapour pressure	1.09 x 10^{-5} mm Hg @ 20°C
Log octanol/water partition coefficient (Log Kow)	6.18
Boiling point	332°C
Melting point	220°C
Flash point	242°C
Solubility in water	0.005 ppm @ 25°C
Chemical stability	Stable under normal temperatures and pressures

The waste treated during the engineering trials was a dry, crystalline material containing primarily HCB. The material was approximately 84 percent HCB, with a yellowish discolouration. The HCB waste was stored in polypropylene bags, which were in turn packed into polypropylene-lined drums. An orange dust was noted between the bag and the inside of the drum. The quantity in each drum ranged from 117 to 254 kg of HCB waste. The test program involved three separate test runs of 3, 9 and 27 drums, processing 514, 1,584 and 4,610 kg of HCB waste, respectively.

Waste handling and TRBP treatment

The HCB waste was delivered to the site in full 205 litre drums contained in secondary containment. Each drum was removed from the secondary containment and immediately weighed. Following weighing, the drums were treated in batch mode using the TRBP. The tops of the drums were removed and the drums placed in the TRBP trays. Once the TRBP trays were loaded with the desired input, the chamber doors were closed and the TRBP operated as per standard operating procedures. Any drums that were only partially filled with HCB crystals were punctured with holes above waste level and connected to a sparger device. These hot hydrogen spargers were used to volatilise the solid waste, and the vaporised contaminants were continuously carried from the TRBP into the GPCR reactor by a sidestream of recirculation or hydrogen gas.

Once the TRBP cycle was complete, the TRBP was cooled to an interior temperature of less than 150°C before unloading (as per current procedures and for safety considerations in handling). The treated drums were then removed from the TRBP using a forklift and placed in the treated material storage area to be tested for regulatory compliance.

System efficiency results

Mass reduction efficiency

The ability of the TRBP to effectively volatilise organics from the input waste drums (mass reduction) was determined by comparing the weight of HCB waste material input, with the weight of the treated solids. Table 2 provides the mass of the input waste and treated waste for each run, and the amount of material volatilised as a percent of the input. Also included in Table 2 are the amounts of HCB and chlorobenzene volatilised from the input waste over the three runs.

Table 2. Reduction of HCB waste constituents in the TRBP

Measurement	Test 1	Test 2	Test 3
Waste Input (kg)	514	1584	4610
Treated Solids	2	23	94
TRBP Mass Reduction (%)	99.61	98.55	97.96
HCB Reduction (%)	99.9999974	99.9999938	99.9999922
Chlorobenzene Reduction (%)	99.9999897	99.9999863	99.9999869

The mass reductions experienced for the three tests were very high at 97.9 to 99.5 percent, and showed a decrease in reduction with increasing waste input quantity. Somewhat higher mass reduction may be realised through longer soak time and/or increased TRBP temperatures during treatment of higher waste quantity loads. Volatilisation of HCB and chlorobenzenes from the input waste was in excess of 99.9999 percent.

Destruction Efficiency

Destruction and Removal Efficiency (DRE) is the measure of the quantity of a contaminant input to the reactor, which does not exit the system as gas. Destruction Efficiency (DE) is the measure of the quantity of a contaminant input to the reactor that does not exit the system in any of the system outputs (including scrubber water). DRE and DE calculations for HCB waste treatment were made using the following formulae:

DRE = 100 x [1 - (total contaminant mass in stack gas)/(total contaminant mass input to reactor)]

DE = 100 x [1 - (total contaminant mass in all outputs)/(total contaminant mass input to reactor)]

Results of DRE and DE calculations are provided in Table 3, and show at least 99.9999 percent ("six-nines") destruction of HCB and chlorobenzenes in the GPCR reactor. DEs could not be calculated for Tests 1 and 2, as there was no effluent produced during the period of the stack sampling.

Table 3. HCB and chlorobenzene DRE and DE results

Test	Destruction and Removal Efficiency (%)		Destruction Efficiency (%)	
	HCB	Chlorobenzenes	HCB	Chlorobenzenes
1	99.999999	99.9999	--	--
2	99.999999	99.9999	--	--
3	99.99999	99.9999	99.99999	99.9999

The DREs for HCB were better than the industry standard of 99.9999 percent for all tests. The DRE for chlorobenzenes also met the technology evaluation standard. The DE results for Test 3 indicates that the water treatment system can reduce contaminants in the effluent to a level where the contribution to the total process outputs does not reduce the overall efficiency of the system.

Summary of test program and GPCR applications

Results of the trials indicated that the system can effectively desorb approximately 98 percent of the waste input to the TRBP. In excess of 99.9999 percent of the HCB and chlorobenzene present in the waste were volatilised in the TRBP and swept to the reactor for destruction. Destruction efficiency measurements indicated at least 99.9999 percent destruction of HCB and total chlorobenzenes. The results of the testing showed that HCB can be effectively destroyed at full-scale commercial throughput rates using Eco Logic's GPCR Process.

In addition to completing the HCB work described above and other waste treatment operations at Kwinana, which are representative of "legacy" waste treatment issues (that is, hazardous waste that has been generated and stockpiled), Eco Logic is pursuing work that uses the GPCR technology for pollution prevention. The technology can be implemented at a small scale for use in manufacturing processes that create organic pollutants including HCB, dioxin, PCBs, etc. The technology can be used to treat the waste directly, or, in the case where the waste stream consists of large volumes of liquids or gas, the stream can be carbon filtered and a small GPCR plant used to both treat and regenerate the carbon filters.

Another new application that Eco Logic is pursuing is the treatment of contaminated soil and sediment. The current full-scale GPCR configuration allows for treatment of up to 150 tonnes per month (1,800 tonnes per year) of liquid waste and bulk solid material including drummed material, electrical equipment, contaminated concrete, etc. Eco Logic has teamed with Torftech Inc., who provides a high-throughput front-end system for desorbing contaminants (including HCB) from soil and sediment, at rates from 0.5 to 10 tonnes per hour (3,500 to 70,000 tonnes per year). Both the TRBP and TORBED front-end systems can be attached to a single GPCR reactor system, to provide the flexibility needed to treat the variety of waste matrices characterising hazardous waste stockpiles and contaminated sites.

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