ALTERNATIVES FOR PERSISTENT ORGANIC POLLUTANTS (POPs) DISPOSAL

IPEN Factsheet

It is a common sense approach to prioritize the use of alternative non-combustion technologies* for the disposal of Persistent Organic Pollutants (POPs), over combustion technologies that become new sources of un-intentional releases of POPs. In fact Stockholm Conventionon on POPs, done at Stockholm on May 22, 2001, which entered into force on May 17, 2004; which is an international law, fully supports this approach. Article 5(c) of the Convention states that, parties to the Convention are obliged "to promote" processes and "to prevent" the formation and release of chemicals such as dioxins, furans, polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB). Article 5(d) & (e) of the Convention oblige the parties "to promote" the use of best available techniques (BAT) and best environmental practices (BEP) for prevention and reduction of POPs releases from new sources[1]. The Convention very specifically also clarifies that the word "best" in BAT & BEP means "most effective in achieving a high general level of protection of the environment as a whole"[1].

The alternative non-combustion technologies not only prevent the formation and release of un-intentional POPs, but the capital and operating costs are also considered to be far less compared to incinerators that are equipped with state-of-the-art pollution control devices and monitoring.[2]

Generally, these technologies use physical and chemical means of converting POPs/POPs wastes to less harmful substances. Both the "Destruction Efficiency (DE)" and the "Destructive and Removal Efficiency (DRE)"** of these technologies for POPs have been evaluated and reported by agencies such as FAO[3], Environment Australia[4], the US Department of Defense[5] and the Department of Energy[6].

There are commercialized non-combustion technologies with operating plants licensed to destroy stockpiles high in POPs concentrations, specifically noting the following: Gas Phase Chemical Reduction (GPCR), Base Catalyzed Decomposition (BCD), Sodium Reduction (SR) and Super-Critical Water Oxidation Reduction (SCWO)[7]. These commercialized non-combustion technologies are briefly described and discussed here.

Gas Phase Chemical Reduction (GPCR)

This technology probably has the best track record among non-combustion destruction technologies and has been in use for managing POPs wastes for the past eight years[7]. In GPCR process, the POPs destruction reaction takes place in a reducing atmosphere devoid of oxygen, where dioxins are not likely to be produced and the dioxins in wastes would also be decomposed [3,8,9]. The process is based on the gas phase thermo-chemical reduction reaction of hydrogen with organic and chlorinated organic compounds. At 800 to 900 °C and low pressure, hydrogen reacts with compounds like PCBs, DDT, HCB & pesticide mixtures, reducing these mainly to methane & hydrogen chloride and minor amount of light hydrocarbons. Hydrogen chloride is neutralized with sodium hydroxide and recovered as sodium chloride. As the reaction with hydrogen occurs in the gas phase, pre-treatment is necessary for both solid & liquid wastes. Pre-treatment technologies have been developed and are commonly used. Solid waste is treated directly without any size reduction or shredding[7,10,11].

Depending upon the strength of the waste and pre-treatment facility, up to 100 tons of waste per day can be disposed of by GPCR technology. This destruction technology can be applied to all POPs, including wastes with high POPs concentrations, PCBs transformers, capacitors and oils[7,11].

GPCR Process Performance:

This process has been reported to demonstrate high destruction efficiencies (DE) for HCB, PCBs, dioxins/furans contaminated wastes and mixed chlorinated pesticides. In commercial scale performance tests in Canada, DEs of 99.999% have been reported for PCBs and HCB. Dioxins/furans which were present as contaminants in the PCBs oils were also destroyed by this process with DE of 99.999%. Similar tests carried out in Japan to evaluate the destruction of dioxins/furans in wastes by GPCR process, have also shown high DEs of 99.9999%[7,11].

Environmental Consideration:

In GPCR process all emissions and residues may be captured for assay and reprocessing if so desired[7,11]. Residues generated by the process include product gas, scrubber water, grit and sludge from the product gas treatment. Dioxins/furans have not been detected in the product gas from GPCR process. In Canada, no uncontrolled emissions, resulting from the application of this process for destruction of PCB-containing material have been reported[13].

This technology has been commercially licensed and used in Australia, Japan and Canada. Furthermore, in the Slovak Republic a new demonstration project is planned for destruction of POPs by GPCR process[7].

Based Catalyzed Decomposition (BCD)

This technology has been employed to treat high strength POPs wastes contaminated with DDT, PCBs, dioxins and furans. BCD is a revised and new version of Base Catalyzed Dechlorination process which was earlier developed by USEPA to remediate soils and sediments contaminated with chlorinated organic compounds[14].

In a BCD process, the solid or liquid waste is heated to 300 to 350 °C under nitrogen atmosphere at normal pressure within the presence of a mixture of high boiling point hydrocarbon, sodium hydroxide and a catalyst. During the process the highly reactive atomic hydrogen produced from the heated mixture, decomposes the organochlorines and other wastes, forming inorganic salts, inert residue and water. The catalyst used in BCD, is then separated from the residue, recovered and reused[7,8,15].

Up to 20 tonnes per hour of contaminated solid waste and 9000 liters of liquid per batch can be disposed off with BCD technology. Smaller units based on BCD process have been developed. Contaminated soils or sediments require some pretreatment such as thermal desorption prior to BCD. This technology is most commonly used for liquid wastes[7].

BCD Process Performance:

From the old BCD plants measurable discharges of organochlorines and dioxins to air were observed but in the modified plants, DREs >99.99999% for 30% DDT input and >99.999999 for 90% PCBs input have been reported[16]. In trail operations, high DEs have been reported for HCB, DDT, PCBs, dioxins & furans[7].

Environmental Consideration:

In the BCD process, all emissions and residues may be captured for analysis and reprocessing if so desired. BCD technology is generally considered to be a low risk technology[7]. The dioxin and furan stack gas emissions in PCBs waste destruction by BCD technology, have been reported to be very small compared to other combustion technologies. BCD technology was used for the destruction of 42,000 tons of stockpiled PCB contaminated soil[17]. Similarly, this technology was applied for dioxin decontamination of highly polluted Spolana Neratovice site in the Czech Republic. Unfortunately, the already decontaminated sludge and used oil agents were consequently burned at the waste incinerator operated by SITA Bohemia in the Czech Republic[18].

This technology has been commercially licensed in Australia, USA, Mexico, Spain, Czech Republic and neighbouring CEE countries[7].

Super-Critical Water Oxidation (SCWO)

In this technology, the unique properties of super critical water (with temperature > 374 °C and pressure > 22 MPa) are employed for complete oxidation and decomposition of toxic organic substances and wastes. The problems of reliability and corrosion of plant material were constantly encountered in the earlier systems. They have now been effectively addressed with the use of anti-corrosion materials and special plant designs. A commercial scale plant based on SCWO process is currently operating in Japan. After an effective demonstration at a pilot and development scale, this process has been recently approved for full scale development and use in the USA[7,12,19].

Super critical water is known for having extremely good characteristics as an oxidation decomposition reaction catalyst, by freely dissolving organic material and oxygen[10]. SCWO is a high temperature and pressure process, carried out in a compact totally enclosed system, in which temperature at 400 - 500 °C and pressure at 25MPa, the oxidation proceeds rapidly to completion. Decomposition products include carbon dioxide, water and inorganic acids or salts. The system is limited to treatment of liquids and solids with an organic content < 20% and solids with diameter < 200 microns. High content PCBs wastes make the residual contents of the process acidic (low pH), and to avoid the resulting corrosion of plant material and attached pipes, it is neutralized by the use of alkali[12,19].

Current demonstration plant units based on SCWO are of 400 kg/hour capacity, and there are plans to enhance the capacity to 2700/hour. SCWO has been employed for the disposal of a broad range of materials, including all POPs, industrial organic chemicals, agricultural chemicals, and explosives. SCWO has also been used for the treatment of a wide range of contaminants such as aqueous waste streams, sludge and waste water, contaminated with PCBs, pesticides, cyanide, halogenated aliphatics and aromatics[10,12].

SCWO Process Performance:

Destruction and removal efficiencies (DREs) > 99.99994% for thetreatment of dioxins contaminated wastes and > 99.999% for treatment of numerous hazardous organic compounds (including chlorinated solvents, PCBs and pesticides), by SCWO technology have been reported[12,20]. Bench scale testing has demonstrated the potential for high destruction efficiencies of POPs by this technology[7].

Environmental Consideration:

In SCWO process, all emissions and residues may be captured for analysis and reprocessing if so desired[7]. The gaseous emissions are not considered significant, noting carbon monoxide level < 10 ppm, nor do they contain particulates, nitrogen oxides, hydrogen chloride or sulfur oxides[21]. Recent study showed that PCDD/Fs formation can occur under specific conditions during PCB destruction at this technology[22], so it requires mandatory monitoring of POPs releases and proper and fully controlled operation.

Sodium Reduction (SR)

This technology is considered well established and has been used commercially for a number of years for treating both low and high concentrations of PCBs contaminated oils. The technology is transportable and widely employed for on-site removal of PCBs from active transformers[7].

In the SR process, chlorine from PCBs is completely removed by alkali metal reduction, with dispersed sodium in mineral oil. The dechlorination process is carried out by agitating the reactant mixture under a dry nitrogen atmosphere at normal pressure. Metallic Sodium size, its concentration and optimum reaction temperatures vary with the type of SR process employed. Pretreatment includes the removal of moisture from the reagents. At the end of the reaction, excess sodium is removed with the addition of water. In SR processing there is a minimum amount of solid residues formed. By-products include water, sodium chloride, sodium hydroxide, and biphenyls. Treated oil may be reused[8].

A mobile plant based on SR technology with the capacity to dispose of 15,000 liters/day of oil, has been in use for PCBs contaminated transformer oil[7]. Destruction efficiency (DE) values of greater than 99.999 percent and destruction removal efficiency (DRE) values of 99.9999 percent have been reported for chlordane and hexachlorobenzene. For other POPs DE as well as DRE related to the SR process have not been reported. Whereas, the emissions of nitrogen and hydrogen are likely, the information on organic emissions is also lacking. However, SR processing for transformer oil treatment has been successfully demonstrated to meet the regulatory criteria in USA, EU, Canada, Australia, Japan and South Africa. This technology is widely available worldwide[7].

Other Non-combustion Technologies

Non-combustion technologies for POPs waste destruction are a challenging area where new technologies are developed but there is limited knowledge and implementation of such technologies. There are more technologies available in full commercial scale (for example in continuous mode by closed circuit CDP process used for on site clean up of PCBs transformers in Cyprus[24]) and some promising technologies which can be used in the future, for example for clean up of PCDD/Fs contaminated incinerator fly ashes as well as for PCBs containing wastes (based on different catalysts reactions[25,26]).

In the recently concluded meeting of the Basel Open Ended Working Group on “Basel Guidelines on POPs Wastes,” the group agreed to recommend that the technologies applied should be capable of achieving a destruction efficiency (DE) of 99.9999%, when these are operating with waste consisting of or containing POPs with a POP content > 1%. The group also agreed to recommend, among others, the technologies described above, GPCR, BCD, SCWO and SR to be classified as “Environmentally Sound and Commercially Available[27].” Recent study also recommends to prepare evaluation of POPs disposal technologies based on full TEQ (including both its elements: PCDD/Fs and PCBs in TEQs) evaluation which will include both PCBs and PCDD/Fs formation.

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IPEN Dioxin, PCBs and Waste Working Group

The IPEN Dioxin, PCBs and Waste Working Group was established in May 2001 in Sweden, after the text of the Stockholm Convention was agreed. The Working Group, within its capacity and resources, works to assure that measures addressing dioxins, PCBs and wastes are appropriately interpreted and fully incorporated into each country's Stockholm Convention Enabling Activities and National Implementation Plans. Furthermore, it works to promote policies and practices in every region and country aimed at the elimination of dioxins and PCBs; and aimed at the reduction and elimination of wastes, and appropriate waste management for residues.

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* Non-Combustion Technologies: The processes which operate in a starved or ambient oxygen atmosphere.

** Destruction efficiencies (DE) are determined by considering the occurrence of undestroyed chemicals of concern in all gaseous, liquid and solid residue. Destruction and removal efficiencies (DRE) are determined by considering only gaseous residues.