

# NON-COMBUSTION TECHNIQUES FOR POPS WASTE DESTRUCTION: AN IPEN BRIEF ON ENVIRONMENTALLY SOUND MANAGEMENT OF POPS

This brief describes proven, commercially available non-combustion techniques for Persistent Organic Pollutants (POPs) destruction that have been assessed by UN experts as suitable for developing countries and outlines the problems of using combustion methods such as incineration to attempt to destroy POPs. Implementation of non-combustion techniques for the destruction of POPs has never been more important. Despite the requirements of the Stockholm Convention to destroy or irreversibly transform POPs so that they no longer exhibit POPs characteristics, vast stockpiles of the original 12 POPs still have not been destroyed – particularly PCB oils and equipment.<sup>1</sup>

The addition of 16 new POPs since the entry into force of the Convention has resulted in massive new stockpiles of POPs waste requiring destruction. In future, more of these dangerous chemicals are expected to be listed for destruction and there will be more stockpiles that require management. Current stockpiles include large volumes of plastics impacted with brominated flame retardants and SCCPs, end of life products with high levels of PFAS and polystyrene impacted with HBCD.

Many governments are investigating how to destroy these stockpiles. The available techniques can be divided into two groups: *Combustion* and *Non-combustion*. The most important difference is that combustion processes generate POPs unintentionally by burning POPs waste thereby undermining the objective of the convention, while ***non-combustion plants operate by chemical or mechanical means and DO NOT GENERATE MORE POPS.***

**Combustion technologies must be avoided. They include:**

- **Incinerators (mass combustion, pyrolysis, gasification, plasma arc)**
- **Cement kilns**
- **Metallurgy plants**

The main problems with combustion technologies are the generation of unintentional POPs (UPOPs) such as chlorinated dioxins and furans, which can be emitted to air and released in the flue gas cleaning residues from the combustion plant. Incinerators also release dioxins through their ash residue, which is leading to contamination of the food chain.<sup>2</sup> Cement kilns have emission filters that are very basic compared to incinerators and experience variations in temperatures and excess oxygen, increasing the risk of UPOPs formation and POPs emissions. Cement kilns have no rapid quench system to cool flue gases and reduce *de novo* synthesis of dioxins.<sup>3</sup> Quenches are used as a basic requirement in hazardous waste incinerators for this purpose. Recently, a modern cement kiln in Austria burning HCB waste contaminated the Görtschitztal valley in Kärnten, resulting in HCB being found in fodder, cattle, milk and humans, hundreds of dairy cattle were killed to prevent the production of contaminated milk and 800 tons of dairy products ruined.<sup>4</sup> Metallurgy plants are also a known source of UPOPs (especially dioxin)<sup>5</sup> and should be avoided for burning of POPs waste as they also have similar limitations to cement kilns in terms of pollution controls. Waste incinerators, cement kilns and metallurgy plants are all listed in the Stockholm Convention's

1 83% of all PCB have not yet been destroyed despite a 2028 deadline for destruction. UNEP (2017) PCB a Forgotten Legacy? 2028: Final Elimination of PCB. <http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-PCB-TOR-PEN-2017.English.pdf>

2 <https://ipen.org/documents/toxic-ash-poisons-our-food-chain>

3 Ming-Xiu Zhan, Shuping Pan, Ivan Deviatkin, Tong Chen and Xiao-Dong Lid Thermal reaction characteristics of dioxins on cement kiln dust. *RSC Adv.*, 2018, 8, 3582–3591

4 Weber, R., Schlumpf, M., Nakano, T. *et al. Environ Sci Pollut Res* (2015) 22: 14385. <https://doi.org/10.1007/s11356-015-5162-7> & <https://link.springer.com/article/10.1007/s11356-015-5162-7>

5 Buekens, A., Stieglitz, L., Hell, K., Huang, H. and Segers, P. (2001) Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry. *Chemosphere* Volume 42, Issues 5–7, February 2001, Pages 729–735 [https://doi.org/10.1016/S0045-6535\(00\)00247-2](https://doi.org/10.1016/S0045-6535(00)00247-2)

Best Available Techniques / Best Environmental Practices (BAT / BEP) dioxins toolkit<sup>6</sup> as known sources of dioxin emissions and releases.

To avoid the perpetuation of POPs generation it is critical for countries to adopt non-combustion technology to destroy POPs waste. Some of the best developed, commercially available non-combustion techniques are described below. This list is not exhaustive but represents those technologies that have been extensively operated and proven commercially.

### **GAS PHASE CHEMICAL REDUCTION (GPCR)**

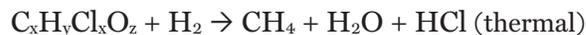
GPCR was initially developed in the 1980s in Canada and operated at laboratory scale before being commercialized and operated at full commercial scale in the 1990s. A large-scale facility in Kwinana, Western Australia operated for 5 years during the 1990s successfully, destroying that state's entire stockpile of PCB and much of Australia's POPs stockpile. The same technology was developed further and later established at pilot and commercial scale in Canada, USA and Japan and has the demonstrated capability to destroy all POPs to high destruction efficiency (DE) levels.

GPCR technology is based on the use of hydrogen at elevated temperatures (approx. 875°C) and low pressure to achieve thermochemical reduction of organic compounds. The contaminated bulk solids material is placed in a sealed chamber called a Thermal Reduction Batch Processor (TRPB), where the POPs are thermally desorbed and carried into the reactor by the heated hydrogen gas. Liquid POPs are preheated and injected directly into the TRBP. Bulk contaminated soils and sediments are processed in a TORBED Reactor System, a modified version of the TRPB allowing higher throughput. Pre-treatment of some wastes is necessary and the system requires electricity, hydrogen, water, and caustic for scrubbing. The 3rd generation of the technology (developed by Hallett Environmental & Technology Group Inc., Ontario, Canada) can also generate energy from excess hydrogen-rich methane process gas that significantly exceeds the parasitic requirements of the process<sup>7</sup> and allows energy export. The reactions that occur generate methane and subsequently the methane is converted to hydrogen gas in a self-regenerating, recirculating process gas system.

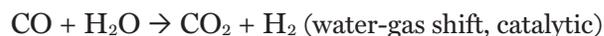
<sup>6</sup> Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on Persistent Organic Pollutants. [http://toolkit.pops.int/Publish/Main/II\\_01\\_Waste.html](http://toolkit.pops.int/Publish/Main/II_01_Waste.html)

<sup>7</sup> This refers to the energy required to run the technology.

The general chemistry of conversion of a hydrocarbon structure containing chlorine and possibly oxygen can be expressed in the following way:



Methane is converted into hydrogen via the steam reforming and gas-water shift reactions, which are expressed as follows:



The process residues include scrubber liquor and water that is suitable for industrial discharge, and solid materials (metal drums, etc.) that are decontaminated and suitable for landfill. Emissions are primarily hydrogen chloride, methane and other hydrocarbons, including benzene. An online mass spectrometer can analyze all reactor exit gases to ensure full dechlorination, and the gases, following scrubbing of the hydrogen chloride, can then be recirculated fully or split between the reactor and boiler fuel feed. The system can operate in modular, transportable and fixed modes, including transportable TRBPs to deal with on-site decontamination of POPs impacted sites.

A double TRBP system can process around 75 tons of solids per month. Liquid inputs can be processed at 2-4 liters per minute. A semi-mobile TORBED reactor can process around 300-600 tons per month. The main advantages are complete destruction of all POPs, self-regeneration of hydrogen process gas, mobility and small footprint (1000m<sup>2</sup>) for systems with a 70 tons/month throughput for smaller stockpiles or contaminated sites, low amounts of solid process residual and a long history of successful commercial utilisation. Recent cost estimates for establishing a GPCR plant are around USD 50 million to construct and USD 1 million to train personnel.<sup>8</sup> This is around 10% of the cost of a modern waste incinerator.

### **SUPERCRITICAL WATER OXIDATION (SCWO)**

Both supercritical and subcritical water oxidation systems have been developed by a number of companies over the last 30 years and some have substantial commercial experience in destroying POPs such as PCB. The technologies share similar principles of destruction of organics using an oxidant agent such as hydrogen peroxide, oxygen or nitrite. The term "supercritical" refers to the state of water just prior to its phase change from liquid to gas under heat and

<sup>8</sup> pers comm Hallett Environmental & Technology Group Inc. 2018

pressure (e.g. 374°C and 218 atmospheres). Subcritical water refers to the state of water just below its critical level (e.g. 370°C and 262 atmospheres). In this state organic materials can be rapidly oxidized and decomposed. For destruction of PCB typical reaction conditions are: temperature 400 - 500°C, pressure 25MPa, with a reaction time of 1 - 5 mins.

Supercritical systems are generally injected with the waste along with water and oxygen into a column; mixed, heated and compressed to the point of supercriticality. The system is totally enclosed. The properties of the water in this phase have elevated molecular kinematic energy that is highly reactive and, combined with oxygen, can oxidize and destroy organic waste. The outputs of the reaction are nitrogen, water and carbon dioxide. The destruction of chlorinated POPs results in an output of elevated hydrochloric acid. The highly acidic environment this generates requires the structural equipment of the process vessels to be corrosion-resistant, such as titanium alloys in combination with anti-corrosive additives such as sodium carbonate. The process is not suited to bulk solids but can treat aqueous wastes, oils, solvents, slurries, and solids with a diameter less than 200 µm. Early versions of the technology were prone to corrosion but this has been resolved with the use of corrosion-resistant materials.

As of 2013 there were 3 fully operational plants, 5 constructed and 9 planned for construction. In the interim, many of these plants will have become operational. The longest established plant is operated in Japan by Japan Environmental Safety Corporation (JESCO) for PCB destruction, with a capacity of 2000 kg of PCB per day (Marrone *et al.* 2013). While costs can vary significantly due to the capacity and type of SCWO developed, a study by Aki *et al.* (1998) found that destruction of hazardous waste from the petrochemical industry could be achieved at significantly lower costs by implementing SCWO rather than by using incineration. Installation costs were 15% less expensive and running costs for SCWO were only around 10% of the costs of incineration of hazardous liquids. SCWO is now used extensively by the US military for destruction of hazardous wastes and chemical weapons, including mobile ship-based units. Marrone, in summarizing a comprehensive review of the global state of SCWO, notes that “SCWO technology commercialization remains an area of great interest and activity.” The main advantages of SCWO are very low emissions, low costs, high DE and low associated resources (catalysts) for operation in remote locations.

## HYDRODEC

The Hydrodec system was a technology developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia for the refurbishment of transformer oil and simultaneous destruction of PCB, and was originally known as catalytic hydrogenation. The company “Hydrodec” was established in 2004 and commenced operations in Australia. The Australian plant currently processes 6.5 million liters of oil a year and the US plant 45 million liters per year. A similar process in Japan can treat 2 tons per day of pure PCB with DE of 99.9996~99.9999%. (Vijgen 2008).

According to the Australian technology developers,<sup>9</sup> the Hydrodec process is based on the mild hydrogenation of spent oil in a packed bed catalytic reactor (hydrogen gas and palladium on carbon (Pd/C) catalyst dispersed in the paraffin oil), operating at moderate temperatures and pressures. Under process conditions hydrogen reacts with heteroatoms in the oil itself, and also with any organochlorines present. Noble metal catalysts are effective but are known to be easily poisoned by contaminants such as sulphur in the oil. Hydrodec developers overcame this issue by using a proprietary additive that scavenges the hydrogen chloride and ensures that the hydrochloric acid produced does not lead to degradation of the catalyst, and which reduces hydrocarbon cracking reactions on the surface of the catalyst. After a program of catalyst and process optimization, it was possible to keep the hydrocarbon structure of transformer oil essentially unchanged, while achieving better than 99.999% destruction of PCB (Duffy and Fookes 1997). While the commercial application for the process is PCB destruction and PCB-free transformer oil rejuvenation, it has been trialed on a range of POPs (see table below) with high DE results and is considered applicable to most POPs in liquid form.

Compound	Feed Concentration (mg/kg)	Product Concentration (mg/kg)	Destruction Efficiency (%)
PCB	40,000	< 0.027	> 99.99993
DDT	40,000	< 0.004	> 99.99999
PCP	30,000	< 0.003	> 99.99999
HCB	1,340	< 0.005	> 99.9996
1,2,3,4-TCDD	46	< 0.000004	> 99.99999

<sup>9</sup> Duffy, G.J. and C.J.R. Fookes, 1997. Development of a Catalytic Process for the Regeneration of Transformer Oils and the Destruction of Chlorinated Hydrocarbons. Presented at the I&EC Special Symposium, American Chemical Society, Pittsburgh, Pennsylvania, September 15-17, 1997.

The emissions from the hydrodec process consist of purge gases that are subjected to two stages of caustic scrubbing to remove acid gases such as H<sub>2</sub>S and HCl. The purge gas is then passed through a catalytic combustor to burn residual hydrogen and any non-condensable hydrocarbons (methane, ethane) formed in the process (Duffy and Fookes, 1997). Chlorine contaminated effluents are scrubbed with caustic solution. Therefore, another process stream is the aqueous waste containing metal chlorides (as result of the neutralization of HCl formed). Such wastewater from the process is collected and disposed of, but in the immediate future it is proposed that wastewater will be treated within an on-site wastewater treatment plant by ozomolysis and ion exchange, which will allow treated water to be recycled in the process (UNIDO 2007).

### BASE CATALYZED DECHLORINATION (BCD)

BCD was developed jointly between the US Navy and the US Environmental Protection Authority (US EPA) to decontaminate liquids, soils, sludge and sediments contaminated with chlorinated organic compounds, especially PCB, dioxins, and furans. The BCD process has received approval by EPA's Office of Toxic Substances under the TSCA<sup>10</sup> for PCB treatment (UNIDO 2007). The technology patent was then passed on to developers and held by BCD Group USA and licensed to operate in the US, Australia, New Zealand, Mexico, Japan, Spain, and the Czech Republic.

Base Catalyzed Dechlorination technology is a two-step process. The first step is to use indirect thermal desorption (direct thermal desorption leads to excessive contaminated off gas that is expensive to treat) to extract POPs from the matrix it contaminates such as building rubble, soil or sediment using a continuous process. The second step is to take the concentrated or pure POPs desorbed in the first step and treat them in a batch process, destroying the POPs in a heated, stirred liquid reaction vessel. This step involves a hydrogen transfer reaction. A carrier oil acts as a hydrogen donor and suspension medium for sodium hydroxide. The oil is heated to 326°C (NaOH melting point) and the NaOH, a reagent and the POPs concentrate from desorption are added. Under exothermic conditions the hydrogen splits from the donor oil

<sup>10</sup> The Toxic Substances Control Act is a United States law, passed by the United States Congress in 1976 and administered by the United States Environmental Protection Agency, that regulates the introduction of new or already existing chemicals.

and hydrogenates the bonded chlorine of the POPs (assuming chlorinated POPs). In combination with a proprietary reagent, the reaction results in water vapor and sodium chloride. Following assessment of the reaction, the oil and sludge are dumped from the reactor and the oil can be recycled into the next batch process. The sludge can be neutralized for landfilling or used for treating acidic waste water (UNIDO 2007).

Modular, transportable and fixed BCD plants have been built. Throughput capacity for the desorption stage differs according to application and ranges between 100 kg/hr and 20 tons/hr (STAP GEF 2004). BCD reactors are limited by solid contents in the reactor waste and usually treat 1-3 tons per batch and 2-4 batches per day. High destruction efficiencies (4-6 nines or 99.9999%) have been demonstrated for DDT, PCB, PCP, HCB, HCH, and dioxins (PCDD/F). Emissions are very low, as for most batch reactors and indirect desorption units. The total mass of emitted off-gas is orders of magnitude smaller than incinerators or similar directly fired desorption units (STAP GEF 2004). This technology has been demonstrated to treat both high strength POPs and large throughputs of contaminated soil, including heavily contaminated dioxin-impacted soil in Spolana, Czech Republic.<sup>11</sup> The relatively low costs of additives (sodium hydroxide is the major input cost) make this a suitable technology for application in most developing countries.

### BALL MILLING

This technology is a mechanochemical application that combines mechanical impact with chemical reagents to create a reduction reaction for chlorinated substrates such as PCB or pesticides. The objective is to achieve reductive dehalogenation of the POPs waste. The waste contaminated with POPs is placed into the ball mill device with an alkali metal compound that acts as a hydrogen donor and is vibrated vigorously to permit agitation of the steel balls, reagent and waste mix. The process is conducted at room temperature, in closed vessels, and no heating is required. There is no process gas to manage, avoiding the release of hazardous organic compounds. Chlorine in the POPs waste is converted to inorganic compounds called CaCl<sub>2</sub> or Ca(ClOH).

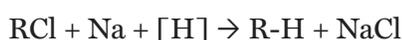
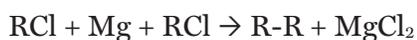
<sup>11</sup> [http://www.recetox.muni.cz/coe/sources/workshop\\_1\\_rba\\_pts/V11-Fairweather.pdf](http://www.recetox.muni.cz/coe/sources/workshop_1_rba_pts/V11-Fairweather.pdf)

The reagents can include calcium oxide (CaO), magnesium (Mg), sodium and other metals, including their oxides. The contaminated material is placed in the ball mill, which is essentially a metal vessel that can operate like batch reactor or even as continuous reactors with the reagent and ball bearings. In addition to PCB and pesticides, it has also been successfully applied to dioxin-contaminated soils. Three commercial applications are well-developed and rely on the same principles: Tribochem's Dehalogenation by Mechanochemical Reaction (DMCR), EDL's Mechano-Chemical Destruction (MCD) and Radical-planet (Research Institute Pty Ltd). Lab-based experiments using ball milling have also proven effective at destroying hexabromocyclododecane (Zhang *et al.* 2014a) and polybrominated diphenyl ethers (Zhang *et al.* 2014b).

One technology vendor (EDL Europe) describes their Mechano-Chemical Destruction (MCD) process:

*“...the ball-to-ball and ball-to-surface collision points are the major regions of fracture and chemical reaction initiation. The reactions induced at the fracture point include radical formation and electron transfer resulting in the destruction of chemical bonds. EDL exploits this chemical phenomena to destroy even the most persistent contaminants which pose a threat to human and environmental health.”*

EDL uses a version of this technology they have patented known as Mechano-Chemical Destruction (MCD) to remediate soils and pesticides. In their version of the technology, an additional central spinning shaft fitted with rotors is included with the main reactor vessel. As the shaft spins it agitates the ball bearings at high speed, leading to a much higher rate of ball-to-ball and ball-to-surface impacts. The chemistry is very complex and relies on radical transformations involving metal-organic radical species. Simplified versions of the reactions are shown below (UNIDO, 2007).



More recently, EDL Europe conducted a joint UNDP/GEF-funded trial remediation of a former US air base in Bien Hoa, Vietnam, treating 150 tons of soil

contaminated with dioxin and dioxin-like PCB. The technology achieved high DE for the dioxin, reducing its levels in soil down to as low as 1000 ppt (1 ppb). A number of other technologies were trialed at the Bien Hoa site to assess suitability for the full-scale remediation of the site. MCD has been short-listed in the selection criteria and cost estimates by comparison with incineration for the dioxin waste were around US \$60 million less expensive for the MCD process, which does not generate UPOPs. They have also completed projects treating pesticides, PCB and dioxins for the US military in Alaska and California, and for the Japanese government and multiple private projects. The first major site remediation was in Mapua, New Zealand which was heavily contaminated with lindane, DDT, dieldrin, and aldrin. The site is now mixed residential and recreational use.

### SODIUM REDUCTION (SR)

This process involves the reduction of PCB using dispersed metallic sodium in a mineral oil carrier. Its main application has been the *in situ* removal of PCB from active transformers, allowing the transformers to continue operation in a decontaminated state without loss of dielectric capability of the mineral oil. Products of this process include sodium chloride, petroleum oils, alkaline water, and polybiphenyls that are no longer halogenated. Both stationary and mobile units are available, with mobile units capable of treating 15,000 liters per day of transformer oil. There are many vendors operating SR systems and most PCB oil with levels above 50 ppm (the regulatory limit for PCB POPs waste) in North America, France, and Germany have been treated using this technology.

In most SR processes, organic liquid containing PCB oil is mixed with a fine sodium dispersion in hydrocarbon oil. Generally, the reaction is run in a standard batch stirred reaction vessel, unless *in situ* treatment is applied (usually in electrical transformers). The technology operates at atmospheric pressure and moderate temperatures, normally between 80 and 180°C. Basic reaction products mainly include various dehalogenated hydrocarbons with higher molecular weight (polyphenyls), sodium halide, and small quantities of hydrogen (UNIDO 2007). The oil products can be reused and the inorganic sludge disposed of. In some cases, solvent extraction may be used as a pre-treatment to remove PCB from porous transformer casings and other adsorbent matrices prior to SR treatment. PCB that are in solid state would need

to be dissolved and removed from the solids prior to SR treatment and must be dewatered. Removal of water is critical due to the high reactivity of dispersed sodium with water, subsequent hydrogen generation and explosive risk. SR is a relatively simple, low emis-

sion, low cost technology with high DE when applied to diluted liquid PCB. The availability and commercialisation are high and the treated PCB oil can be reused at significant cost savings to utility operators and other transformer owners.

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