

Brief Review

of Potential Technologies for Addressing the Issue of Obsolete Polychlorinated Biphenyls (PCBs) and PCB Wastes in Kazakhstan

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1. Introduction

PCBs represent a significant environmental and health hazard in Kazakhstan. In 2010, the basic document for UNDP/GEF project on addressing this issue stated: *“While the initial inventory is far from complete it reveals significant stockpiles of PCBs in Kazakhstan. Altogether 22 companies/sites have approximately 56,000 PCB capacitors in their possession, equalling to 757 tons of PCBs in 2,500 tons of equipment”* (UNDP and Government of Kazakhstan 2010). A large number of transformers with PCB oils was also identified; 106 of them in ArcelorMittal Steel at Temirtau.

As the problem with PCBs commonly occurs in different parts of the country, the non-combustion technology which can be moved easily between sites or can be built as smaller units according to the scale of material which needs to be processed is more suitable for the destruction of PCBs and PCB contaminated soils than the waste incineration or co-incineration.

Of course, other significant criteria need to be considered when choosing the right technology for destruction of PCBs wastes. Some basic steps were suggested in publications by IPEN (IPEN Dioxin PCBs and Waste Working Group 2010) or Costner, Luscombe et al. (1998). The following text describes some of these technologies and their performance levels of destruction of Persistent Organic Pollutants (POPs), a group of chemicals including PCBs.

POPs are globally regulated by Stockholm Convention (Stockholm Convention 2010). Kazakhstan has ratified this convention and prepared National Implementation Plan in order to meet its requirements (Republic of Kazakhstan 2009).

Addressing the problem of sites contaminated by PCBs is a complex issue. Some guidance was provided by Bell (2015) as a part of broader reports prepared by Arnika, EcoMuseum and CINEST (Arnika, AWHHE et al. 2015, Arnika, CINEST et al. 2015).

2. POPs Destruction Efficiency

To assess the performance of technologies used for POPs waste disposal, methods for the evaluation of their Destruction Efficiency (DE) and Destruction and Removal Efficiency (DRE) were introduced.

The destruction efficiency (DE) is the percentage of originating POPs destroyed or irreversibly transformed by a particular method or technology. The destruction removal efficiency (DRE) only considers emissions to air and is the percentage of original POPs irreversibly transformed and removed from the gaseous emissions.

- (1) Both DE and DRE are a function of the initial POP content and do not cover unintentional production of new POPs during destruction or irreversible transformation;
- (2) DE is an important criterion to assess technologies performance for destruction and irreversible transformation, but can be difficult to measure in a reproducible and comparable manner (Basel Convention 2015). The following provisional definition for levels of destruction and irreversible transformation, based upon absolute levels (i.e. waste output streams of treatment processes) should be applied:
 - (a) Atmospheric emissions:
 - (i) PCDDs and PCDFs: $0.1 \text{ ng TEQ Nm}^{-3}$;
 - (ii) All other POPs: pertinent national legislation and international rules, standards and guidelines, examples of pertinent national legislation can be found in annex II;
 - (b) Aqueous releases: pertinent national legislation and international rules, standards and guidelines, examples of pertinent national legislation can be found in annex II;
 - (c) Solid residues: POP contents should be below the low POP contents defined in section A of Basel Technical Guidelines (Basel Convention 2015).

3. Technologies

3.1 Alkali Metal Reduction (Sodium Reduction)

Principle of operation

Reaction of metallic alkali with chlorine atoms contained in the chlorinated compounds

Process description

Alkali metal reduction involves the treatment of wastes with a dispersed alkali metal. Alkali metals react with chlorine in halogenated waste to produce salts and non-halogenated waste. Typically, the process operates at atmospheric pressure and temperatures between 60°C and 180°C (Ariizumi, Otsuka et al. 1997). Treatment can take place either in situ (e.g. PCB-contaminated transformers) or ex situ in a reaction vessel. There are several variations of this process (Piersol 1989). Although potassium and potassium-sodium alloy have been used, metallic sodium is the most commonly used reducing agent.

The process must avoid the formation of a polymer (which occurs in one or two of the technologies identified) or must take the formation of such this solid into account and introduce a separation step to yield the pure reusable oil.

Ex-situ treatment of PCBs can be performed, however, following solvent extraction of PCBs. Treatment of whole capacitors and transformers could be carried out following size reduction through shearing. Pre-treatment should include dewatering by phase separation, evaporation, or another method (UNIDO, 1987) to avoid explosive reactions with metallic sodium. Equipment should be washed with organic solvents. Similarly, the POPs which are solid or in the adsorbed state would need to be dissolved to the required concentration or extracted from matrices (Piersol 1989, UNEP 2004). The process is available in transportable and fixed configurations (UNEP 2000). Mobile facilities are capable of treating 15,000 litres per day of PCBs transformer oil (UNEP 2000).

Performance levels

Destruction efficiency (DE) values of greater than 99.999% and destruction removal efficiency (DRE) values of 99.9999% have been reported for chlordane, HCH, and PCBs (Ministry of the Environment of Japan 2004). Apart from the European Union, the sodium reduction process has also been demonstrated to meet regulatory criteria in Australia, Canada, Japan, South Africa and the United States of America for PCB transformer oil treatment, i.e. less than 2mg/kg in solid and liquid residues (UNEP 2004).

Levels of PCDD/Fs and DL PCBs in different outlets are presented in Table 1.

The highest number of Alkali Metal Reduction facilities is based in Japan. The plants operating in 2006 were treating oils contaminated with polychlorinated biphenyls (PCB). A number of plants treated PCB with concentrations in the range of 100 parts per million, while some plants were treating concentrations up to 10 per cent. In all plants, the exhaust gas was treated with activated carbon (UNEP – EG BAT/BEP 2006).

3.2 Base catalyzed decomposition (BCD)

Principle of operation

The BCD process involves treatment of wastes in the presence of a reagent mixture consisting of hydrogen-donor oil, alkali metal hydroxide, and a proprietary catalyst.

Process description

When the mixture is heated to above 300°C, the reagent produces highly reactive atomic hydrogen. The atomic hydrogen reacts with the waste to remove constituents that confer the toxicity to compounds.

Soils may be treated directly or, more often, different types of soil pre-treatment is necessary: a) Larger particles may need to be removed by sifting and crushed to reduce their size; b) pH and moisture content may need to be adjusted, and c) Indirect Thermal Desorption (ITD) is also used in conjunction with BCD to remove POPs from soils prior to treatment. In these situations, the soil is pre-mixed with sodium bicarbonate prior to being fed into the thermal desorption unit. Water will need to be evaporated from aqueous media, including wet sludge, prior to treatment. Capacitors can be treated following size reduction through shredding. If volatile solvents are present, such as occurs with pesticides, they should be removed by distillation prior to treatment (CMPS&F – Environment Australia 1997).

The equipment associated with this process is readily available (Rahuman, Pistone et al. 2000). Modular, transportable and fixed plants have been built (Vijgen 2002).

BCD has been used at two commercial operations within Australia, one of them still operating. Another commercial system has been operating in Mexico since 1999. In addition, BCD systems have been used for short-term projects in Australia, the Czech Republic, Spain and the United States of America. It was used, for example, to clean up PCDD/Fs and chlorinated pesticides contamination in Spolana Neratovice, the Czech Republic (UNEP – EG BAT/BEP 2006).

Material requirements:

- Hydrogen-donor oil;
- Alkali or alkaline earth metal carbonate, bicarbonate or hydroxide, such as sodium bicarbonate. The amount of alkali required is dependent on the concentration of the halogenated contaminant contained in the medium (CMPS&F – Environment Australia 1997). Amounts range from 1% to about 20% by weight of the contaminated medium; and
- Proprietary catalyst amounting to 1% by volume of the hydrogen donor oil.

Performance levels

DEs of 99.99–99.9999% have been reported for DDT, PCBs, PCDDs and PCDFs (UNEP 2000). DEs of greater than 99.999% and DREs of greater than 99.9999% have also been reported for chlordane and HCH (Ministry of the Environment of Japan 2004). It has also been reported that reduction of chlorinated organics to less than 2mg/kg is achievable (UNEP 2001).

Data on emissions from base catalysed decomposition for two plants operating in Japan, one plant operating in Australia and one plant operating in the Czech Republic were provided to the Stockholm Convention expert group on BAT/BEP (UNEP – EG BAT/BEP 2006) and are summarized in Table 1. The first three plants treated PCB at varying levels up to 10 per cent. It was noted that a former plant which treated soil contaminated with a range of persistent organic pollutants at the Sydney Olympic site in Australia had been decommissioned in 2003.

3.3 Catalytic hydrodechlorination (CHD)

Principle of operation

Hydrogen reacts with chlorinated organic compounds or non-chlorinated organic contaminants, such as PAHs, at high temperatures.

Process description

CHD involves the treatment of wastes with hydrogen gas and palladium on carbon (Pd/C) catalyst dispersed in paraffin oil. Hydrogen reacts with chlorine in halogenated waste to produce hydrogen chloride (HCl) and non-halogenated waste. In the case of PCBs, biphenyl is the main product. The process operates at atmospheric pressure and temperatures between 180°C and 260°C (Noma, Muramatu et al. 2002, Noma, Ohno et al. 2003).

PCBs and PCDDs/PCDFs must be extracted using solvents or isolated by vaporization. Substances with low boiling points such as water or alcohols should be removed by distillation prior to treatment. Biphenyl, the main product, is separated out from the reaction solvent by distillation after the reaction, and the catalyst and reaction solvent are reused for the next reaction (Basel Convention 2015).

The CHD process requires the same number of hydrogen atoms as the number of chlorine atoms in the PCBs, and also 0.5% by weight of the catalyst.

CHD is available in fixed and transportable configurations depending on the volume of PCBs to be treated. In Japan, a plant which is capable of treating 2mg PCB per day using the CHD process was constructed and is in operation. Similar plants are run in Canton, the United States of America and in Young, Australia. In Japan, a commercial-scale plant was constructed at the Japan Environmental Storage & Safety Corporation (JESCO) Osaka facility in 2006 where PCBs extracted from transformers and capacitors are treated by the CHD process (JESCO 2009a).

There are many reports on PCB dechlorination by the CHD process. Generally, Pd/C catalyst shows the largest degradation rate compared to the other supported metal catalysts. The reaction temperature can be increased to 260°C when paraffin oil is used as reaction solvent (Basel Convention 2015).

Waste input IN: CHD has been demonstrated with PCBs removed from used capacitors. PCDDs and PCDFs contained in PCBs as impurities have also been dechlorinated. A vendor has also claimed that chlorinated wastes in a liquid state or dissolved in solvents can be treated by CHD.

Performance levels

DEs of 99.98–99.9999% have been reported for PCBs. It has also been reported that a reduction of the PCB content to less than 0.5mg/kg is achievable (Basel Convention 2015). Levels of PCDD/Fs and DL PCBs in different outlets are presented in Table 1.

3.4 Gas phase chemical reduction (GPCR)

Principle of operation

The GPCR process involves the thermochemical reduction of organic compounds.

Process description

At temperatures greater than 850°C and at low pressures, hydrogen reacts with chlorinated organic compounds to yield primarily methane, hydrogen chloride (if the waste is chlorinated), and minor amounts of low molecular weight hydrocarbons (benzene and ethylene). The hydrochloric acid is neutralized through the addition of caustic soda during the initial cooling of the process gas, or can be taken off in acid form for reuse. The GPCR technology can be broken down into three basic unit operations: the front-end system (where the contaminants are rendered into a suitable form for destruction in the reactor), the reactor (which reduces

the contaminants, now in gas phase, using hydrogen and steam), and the gas scrubbing and compression system (Basel Convention 2015).

Contaminants must be in a gaseous form in order to be reduced in the GPCR reactor. While liquid wastes can be pre-heated and injected directly into the reactor on a continuous basis, contaminants on solids must first be volatilized from the solid. Depending on the waste type, one of the following three pre-treatment units is used to volatilize wastes prior to treatment in the GPCR reactor:

- Thermal reduction batch processor (TRBP) for bulk solids, including those in drums;
- Toroidal bed reactor for contaminated soils and sediments, but also adapted for liquids;
- Liquid waste pre-heater system (LWPS) for liquids.

In addition, other pre-processing is required for large capacitors and building rubble. Large capacitors are punctured and drained, while rubble and concrete must be reduced in size to less than one square meter.

Gases leaving the reactor are scrubbed to remove water, heat, acid and carbon dioxide. Scrubber residue and particulate will require disposal off site. Solid residues generated from solid waste inputs should be suitable for disposal in a landfill.

Methane produced during the process can provide much of the fuel needs. It has been reported that electricity requirements range from 96 kWh per ton of soil treated to around 900 kWh per ton of pure organic contaminants treated.

There is a need for hydrogen supplies, at least during start-up. It has been reported that methane produced during the GPCR process can be used to form enough hydrogen to operate the process thereafter. The hydrogen production unit was plagued, however, by reliability problems in the past. Other material requirements include caustic for the acid scrubber.

GPCR is available in fixed and transportable configurations.

GPCR process capacity is dependent on the capacity of the three pre-treatment units, as specified below:

- TRBP has a capacity of up to 100 tons of solids per month or up to four litres per minute of liquids. Two TRBPs can be used in parallel to double capacity;
- Toroidal bed reactor has a capacity of up to 5,000 tons of soils and sediments per month, although this pre-treatment unit is still in the development stage; and
- LWPS has a capacity of three litres per minute (Vijgen 2002, UNEP 2004).

Commercial-scale GPCR plants have operated in Canada and Australia. The GPCR plant in Australia operated for more than five years until 2000. In the United States, it is planned to build a GPCR synthetic diesel plant with a 200 tons per day capacity in Fauquier County, Virginia.

Performance

DEs of 99.9999% have been reported for DDT, HCB, PCBs, PCDDs and PCDFs.

A Danish review (DANCEE 2004) noted that emissions of PCDD/PCDF from the gas phase chemical reduction process to all media were lower than those from the base catalysed decomposition process. Levels of PCDD/Fs and DL PCBs in different outlets are presented in Table 1.

Table 1: Releases of U-POPs by different alternative technologies to waste incineration as potential alternatives for PCBs containing wastes

Technology	Specific facility	Operation period	Air releases (ng TEQ m ⁻³)	Water discharge (ng TEQ l ⁻¹)	Source
PCDD/Fs and dioxin-like PCBs					
Alkali metal reduction	Japan Environmental Safety Corporation, Kitakyushu facility	Dec 2004–March 2015	0.0000013–0.0000530		(UNEP – EG BAT/BEP 2006)
	Japan Environmental Safety Corporation, Toyota facility	Sep 2005–March 2015	0.0000842–0.0024947	NA	
Catalytic-hydro dechlorination	Japan Environmental Safety Corporation, Osaka facility	2006–March 2015	0.000079–0.00010	NA	(UNEP – EG BAT/BEP 2006)
Photochemical dechlorination and catalytic dechlorination reaction	Japan		0.00007	NA	(UNEP – EG BAT/BEP 2006)
Supercritical Water Oxidation	Japan		0.001–0.002	0.0000005	(UNEP – EG BAT/BEP 2006)
Subcritical Water Oxidation	Japan		0.00009	NA	(UNEP – EG BAT/BEP 2006)
PCDD/Fs only					
Alkali metal reduction	Japan Environmental Safety Corporation, Kitakyushu facility	Dec 2004–March 2015	0		
	Japan Environmental Safety Corporation, Toyota facility	Sep 2005–March 2015	0–0.0015834	0.0000003500–0.0000077500	
Catalytic-hydro dechlorination	Japan Environmental Safety Corporation, Osaka facility	2006–March 2015	0.00000066–0.00000076	NA	
BCD (Australia)	BCD Technologies, Queensland		0.0119–0.05	NA	(UNEP – EG BAT/BEP 2006)
BCD (Japan)	Japan		<0.01	NA	(UNEP – EG BAT/BEP 2006)
BCD (Spolana Neratovice – pilot)	BCD CZ, s.r.o., Prague		0.013–0.031	NA	(UNEP – EG BAT/BEP 2006)
BCD (Spolana Neratovice – full)	BCD CZ, s.r.o., Prague		0.0017–0.0424	0–1.4	(Veverka, Čtvrtníčková et al. 2004)
Gas Phase Chemical Reduction	Australia		0,0000028–0.00027 (<0.016)	0.00000061–0.00084	(Vijgen and McDowall 2008)
DL PCBs only					
Alkali metal reduction	Japan Environmental Safety Corporation, Kitakyushu facility	Dec 2004–March 2015	0.0000013–0.0000530		
	Japan Environmental Safety Corporation, Toyota facility	Sep 2005–March 2015	0.0000842–0.0024947	0.0000372590–0.0001289250	
Catalytic-hydro dechlorination	Japan Environmental Safety Corporation, Osaka facility	2006–March 2015	0.000078–0.00010	0.0000372590–0.0001289250	
PCBs only					
Alkali metal reduction	Japan Environmental Safety Corporation, Kitakyushu facility	Dec 2004–March 2015	<0.000010 – 0.000600 mg m ⁻³	ND (0.003 mg l ⁻¹)	
	Japan Environmental Safety Corporation, Toyota facility	Sep 2005–March 2015	<0.001 mg m ⁻³	<0.0005 mg l ⁻¹	
Catalytic-hydro dechlorination	Japan Environmental Safety Corporation, Osaka facility	2006–March 2015	0.00067–0.0024 mg m ⁻³	NA	

4. Economics

Summarized in the following table:

Table 2: Basic information about financial costs of the non-combustion technologies

Technology	Vendor	PCB Oils	Soils	Capacitors	Transformers
Ball Milling ¹	EDL	\$300/ton	\$250/ton	\$300/ton	\$300/ton
Base Catalyzed Decomposition ²	Multiple	\$0.7–2.2/kg depending on waste	\$300/m ³		
Catalytic hydrogenation ¹	Hydrodec Group PLC	5–50ppm PCB: \$0.40/L 50–500ppm PCB: \$0.80/L >500ppm PCB: \$4.00/L			
Gas Phase Chemical Reduction ¹	Natural Energy Systems Inc.	\$2300/tonne – for 100% PCB waste	\$500/tonne – assumes low % of PCB.	\$1300/tonne – assumes 40% PCB.	\$1300/tonne – assumes 40% PCB.
Solvated Electron Technology ¹	Oasis Systems / Commodore	\$5512–\$6614/tonne	\$5512–\$6614/tonne	\$5512–\$6614/tonne	\$5512–\$6614/tonne
Sodium Reduction ¹	Kinectrics Inc	\$0.9–\$7/litre		\$500–1700/tonne	\$500–1700/tonne
Sodium Reduction ¹	ESI Group	\$0.35 to \$0.85/litre (up to 3000ppm)	\$680 to \$1700/tonne	\$1700 to \$4250/tonne	\$800 to \$1220/tonne

Sources of information: ¹ SNC Lavalin (2008), ² McDowall (2007)



Indirect thermal desorption unit in Spolana Neratovice served for evaporation of persistent pollutants from contaminated debris and soil into processing oil.



BCD facility in Spolana Neratovice for remediation of the dioxin contaminated site.



Muffle furnace in BCD remediation plant in Spolana Neratovice.



Gas Phase Chemical Reduction (GPCR) unit used for remediation in Australia.



Sodium Reduction (SR) facility used for destruction of PCB oils in Philippines.

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