

Name of Process:

Base Catalyzed Decomposition (BCD) formerly called Base Catalyzed Dechlorination

Applicable POPs wastes:

DDT, HCB, PCBs, PCDDs and PCDFs.

BCD should be applicable to other POPs in addition to the waste types listed before (UNEP, 2004; Vijgen, 2002). BCD should be capable of treating wastes with a high POP concentration, with demonstrated applicability to wastes with a PCB content of above 30 % (Vijgen, 2002). Applicable waste matrices include soil, sediment, sludge and liquids. The owners of the process claim that it has been demonstrated to destroy PCBs in wood, paper and metal surfaces of transformers.

Status:

BCD has been used at two commercial operations within Australia, with one still operating. Approx. 8-10,000 t of PCB's and PCB contaminated oils, 25 t of Pesticide chemicals and pesticide waste, 15 t of pesticide concentrates collected from soil remediation

Another commercial system has been operating in Mexico (from 1998 till present treated 1400 tons of liquids and solids with PCB's. BCD systems have been used for short-term projects in Australia, Spain and the United States of America.

A BCD unit for the treatment of both PCDD- and PCDF- contaminated soil and pesticide wastes is tested at pilot scale and the full scale plant has been constructed and working within the Czech Republic. The plant is treating 35,000 t of soil and building rubble contaminated with PCDD/F, HCB & HCH. In addition to treating more than 1000 t of contaminated concentrate from the first stage thermal desorption process more than 200 t of waste pesticide intermediates is also being treated. The full scale plant has been in operation since early 2006.

BCD has been successfully applied in US in the combination with thermal desorption for soil remediation. In Basque Country, Spain another system has been operating from 2000 to 2002 by IHOBE S. A. where 3500 tons of pure HCH waste has been destructed to TCB, which was used by the industry. In the US the BCD system has been successfully applied in combination with thermal desorption at the beginning of the 90's.

In Japan, a continuous process for oils with low contamination of PCB's has been developed.

The patent owners of this technology sell licences to operate the technology. Currently, licences are held by companies based in Australia, Czech Republic, Japan, Mexico and the United States of America.

Technology description:

Based on patents developed at the Cincinnati Risk Reduction Research Laboratory by C. Rogers, A. Kornel and their group from the US EPA, there have been given licenses to various vendors. Initially, the technology was developed for the destruction of halogenated compounds. With the improved chemistry, all heteroatoms other than just chlorinated (Halogenated) compounds are destroyed. For this reason the term Dechlorination in BCD has been modified to "Decomposition".

The BCD process involves treatment of liquid and solid wastes in the presence of a reagent mixture consisting of a high boiling point hydrocarbon such as number 6 fuel oil, sodium hydroxide and a proprietary catalyst. When heated to about 300° C, the reagent produces highly reactive atomic hydrogen, which cleaves chemical bonds that confer toxicity to compounds.

The residues produced from decomposition of heteroatomic compounds are carbon, and sodium salts of anions liberated during the complete decomposition reactions. After the thermal treatment reaction, the inorganic and carbonaceous solids are separated from the unreacted oil by centrifugation and drying. The oil is recovered for reuse in following treatment cycles. If it is desired to further separate the solids residues, the salts and excess base can be removed from carbon residue by washing with water. The carbon residue is non-toxic, has no heteroatoms attached and can be disposed of as any non-toxic material. The BCD process has the advantages of not requiring very high temperatures, high pressure, or energetic reagents.

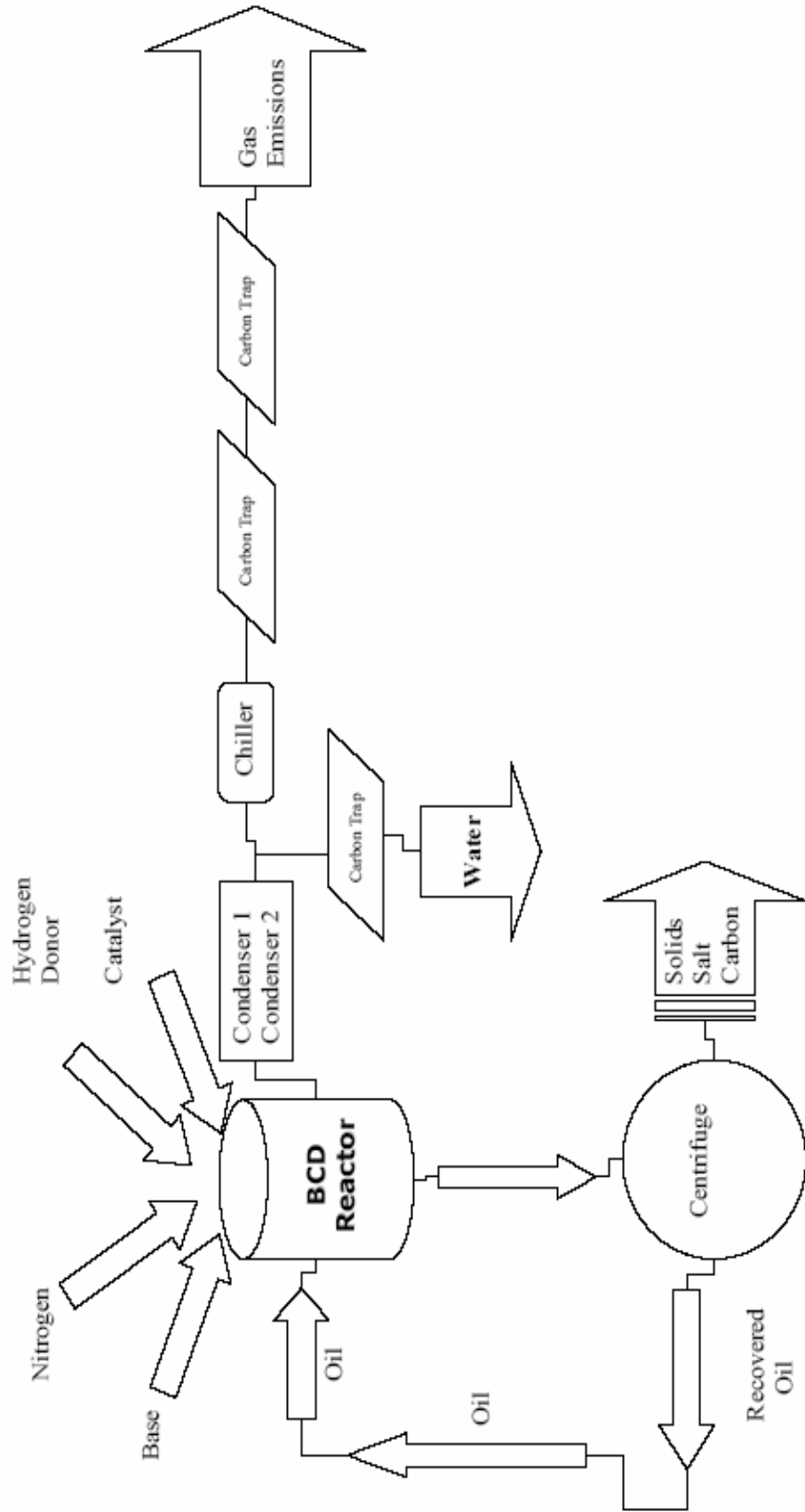
Alternatively, when pesticides or other pollutants are contaminants in soil, sediment or other solid matrices, the BCD process is linked with a pre-treatment step such as thermodesorption to remove, concentrate and collect contaminants. The collected contaminates can be destroyed on-site in a mobile BCD vessel designed to treat liquids (CMPS&F, 1997, HCB Communication, 2000).

In 1997 the BCD inventors C. Rogers and A. Kornel discovered a new more effective BCD catalyst while working as visiting scientists at the USEPA Laboratory in Cincinnati, Ohio. When PCBs in 10% concentrations were treated with the original BCD catalyst, it required up to three hours to effect complete destruction of all PCB congeners. When the newly discovered BCD catalyst is employed, PCBs in 20% concentrations are destroyed within 20-30 minutes (see following Table) and 30% PCB concentrations are destroyed within 60-90 minutes.

In 2004 at the Spolana site in Czech Republic at the trial in the pilot plant, HCB waste with an organic chlorine content of 55%, dioxins in dust up to a level 1,620,000 ng/kg I-TEQ has been successfully destroyed (see under DE). In the full scale plant pesticide wastes with 70% chlorine content are being treated.

BCD Process Flow

Process diagram:



PART I: Criteria on the Adaptation of the Technology to the Country

A. Performance:

Details on performance can be found in the Annex to this sheet in Tables 1-6

1. Minimum pre-treatment:

Soils may be treated directly. Different types of soil pre-treatment may be necessary:

- (a) Larger particles may need to be removed by sifting and crushed to reduce their size; or
- (b) pH and moisture content may need to be adjusted.

Thermal desorption has also been used in conjunction with BCD to remove POPs from soils prior to treatment. In these situations, the soil is premixed with sodium bicarbonate prior to being fed into the thermal desorption unit (CMPS&F, 1997). Water will need to be evaporated from aqueous media, including wet sludge, prior to treatment. Capacitors can be treated following size reduction through shredding (CMPS&F, 1997). Volatile can be presently treated in pressure reactors.

2. Destruction efficiency (DE):

DEs of 99.99–99.9999 % have been reported for DDT, HCB, PCBs, PCDDs and PCDFs. (UNEP, 2004b). DEs of greater than 99.999 % and DREs of greater than 99.9999 percent have also been reported for chlordane and HCB (Ministry of the Environment of Japan, 2004). It has also been reported that reduction of chlorinated organics to less than 2 mg/kg is achievable. (UNEP, 2001), however the vendors claim DE's achievable down to levels below analytical detection.

Latest results of the pilot-scale demonstration at Spolana (M. Kubal et al, 2004)

The efficiencies of destruction of polychlorinated dibenzodioxines and dibenzofuranes (which are the most toxic contaminants monitored) during each run of the BCD reactor were extraordinary high

Dioxin Destruction.

Material:	Inlet ng/kg I-TEQ	Outlet Oil Matrix ng/kg I-TEQ
Chemical waste	209,000	0 (Reported value)
Chemical waste	200,000	4.3
Chemical waste	11,000	0.23
Chemical waste	47,000	0
Chemical waste	35,000	0
Dust	1,620,000	0.52
Chemical waste	78,000	0
Concentrate Aqueous	96,000	0
Concentrate Organic	876,000	0

Destruction of HCB & Lindane.

Material	Inlet mg/kg		Outlet Oil Matrix mg/kg	
	HCB	Lindane	HCB	Lindane
Chemical waste	29,000	1,500	< 1.0	< 1.0
Chemical waste	200,000	900	< 2.0	< 2.0
Chemical waste	550,000	1,000	< 2.0	< 2.0
Chemical waste	270,000	1,000	< 2.0	< 2.0
Chemical waste	160,000	1,000	< 2.0	< 2.0
Dust	7,600	7	< 2.0	< 2.0
Chemical waste	1,598	19,000	< 2.0	< 2.0
Concentrate Aqueous	630	<2.0	< 2.0	< 2.0
Concentrate Organic	11,000	<2.0	< 2.0	< 2.0

The conclusions of the tests in Spolana have been formulated as follows (Kubal et al., 2004):

"The solid waste treatment strategy directed to processing of waste showing extremely high contents of polychlorinated compounds (including dioxins) was successfully presented within the pilot-scale demonstration project at former pesticides producing plant in Spolana Neratovice. The treatment system consisting of thermal treatment unit and a BCD reactor proved its capability to effectively detoxicate soil, concrete, bricks, plaster, steel and dust contaminated by polychlorinated compounds as well as to provide more than satisfactory destruction of these chemicals in their concentrated form. The demonstration results confirmed the ability of these technological processes to clean up the solid waste with extraordinary high efficiency thus providing an effective remediation tool for this heavily polluted site."

Operations as expected give better results in the upstream thermal treatment than the pilot plant. Dioxins are usually less than 0.01 ng/g, HCB and HCH below detection limits and destruction in the BCD reactors confirms the pilot results. Pure HCB wastes have been treated with 70% chlorine content.

3. Toxic by-products:

The by-products are salt containing excess caustic soda and carbon. This material is disposed of to secure landfill without significant toxic properties. In addition there are small amounts of donor oil, free of both organic and inorganic chlorine recycled as fuel to licensed users. USEPA tested extensively for the formation of toxic by-products. None were detected.

4. Uncontrolled releases:

Modern plants are designed with a high degree of intrinsic safety. Vapour release pass through double condensers, chillers and double activated carbon filters before release. Pressure safety valves are routed to a containment tank.

5. Capacity to treat all POPs:

Capacity to treat all POPs. The process is not selective all organically bonded halogen groups are attacked and degraded. An extensive list of pesticides was tested. Direct treatment of capacitors is not possible and solvent extraction is required. Although some facilities shred the capacitors and treat the material with sodium hydroxide. The shredded material can be treated with the BCD process

Compounds treated:

The following have been treated on an industrial scale: all types of PCB's, PCDD/Fs, HCH, including Lindane wastes, HCB, DDT, PCP and other chlorinated phenols.

6. Throughput:

6.1 Quantity [tons/day, L/day]

Latest information in 2004, quoted that both in Mexico and in the Czech republic the BCD reactor has been sized at 10 m³ volume and equipped with thermo-oil heating as against the original small electric heating. The result has been to greatly improve the relative heat up times to increase productivity so that 3 batches per 24 hours are now easily achievable and the overall productivity and throughput of such BCD units now are improved such that up to 1000 t/y of high chlorine content PCB's or pesticides (50%) can now be treated in a single line. The reactor can also treat 2000 t/y of contaminated filter dust and up to 7000 t/y of oils with moderate to low contamination of PCB's

In case larger capacities are required more reactors can be added. Low contaminated oils can be treated at up to 5000 t/y per reactor. Transportable plants are available with 2-5 m³ reactors. 10 m³ reactors relocatable instead of transportable.

Examples:

50% Chlorine can be treated for each single reactor with 3-4 t/day. It is easy to add more reactors per line and the capacity can be multiplied accordingly.

With 5% Chlorine the capacity can be increased as less NaOH is needed up to 6-8 t/day.

Pesticides Waste with 1000 ppm chlorine can be easily treated in the BCD reactors, however if the quantities are large it is technically and financially better to treat such waste

Soil with OCP contents up to 20% have been treated in the thermal desorption step and the resulting concentrates then fed to the BCD reactors. Because of the robustness of the BCD reaction and the ability to treat mixtures with high mineral solids content it is well suited to site remediation problems where contaminated ground and buildings need treatment.

6.2 POPs throughput : [POPs waste/total waste in %]

30% and recently in Spolana up to 55%

7. Wastes/Residuals:

7.1 Secondary waste stream volumes:

Air emissions are expected to be relatively minor. The potential to form PCDDs and PCDFs during the BCD process is relatively low. However, it has been noted that PCDDs can be formed from chlorophenols under alkaline conditions at temperature as low as 150°C (Weber, 2004). It should be mentioned that in the Olympic site project in Australia chlorophenols and PCDD/F were treated at the same time. PCDD/F's were similarly destroyed. The operating temperature was 350 °C.

Other residues produced during the BCD reaction include sludge containing primarily water, salt, unused hydrogen donor oil and carbon residue. The vendor claims that the carbon residue is inert and non-toxic. For further details, users are referred to the literature produced by BCD Group, Inc.

Latest development in 2004 is that the process has the choice of using low cost heavy fuel oils or refined paraffinic oils as the donor oil in the process. Heavy fuel oils can be used once only, with the used oil being fed to cement kilns after destruction of POP's. Where this option is not used it is now possible to recover and re-use 90-95% of the donor oil which greatly improves the economics of the process and reduces the production of wastes virtually to a solids stream of sodium chloride and carbon from the breakdown of the POP molecule.

Latest results at Spolana (Kubal et al., 2004):

Treatment of Solid Matrices in Upstream Desorber:

Dioxin Removal:

Material	Inlet ng/kg I-TEQ	Outlet ng/kg I-TEQ
Soil	46,500	2.9
Brick&Concrete	2,420,000	6.3
Concrete	4,780,000	66.0
Plaster	3,800	5.6

HCB & Lindane Removal:

Material	Inlet mg/kg		Outlet mg/kg	
	HCB	Lindane	HCB	Lindane
Soil	2,643	1.34	< 1.0	< 1.0
Brick&Concrete	49,000	11	< 1.0	< 1.0
Concrete	5,100	18	< 1.0	< 1.0
Plaster	270	< 1.0	< 1.0	< 1.0

Since the BCD process involves stripping chlorine from the waste compound, the treatment process may result in an increased concentration of lower chlorinated species. This can be of potential concern in the treatment of PCDDs and PCDFs, where the lower congeners are significantly more toxic than the higher congeners. It is therefore important that the process be appropriately monitored to ensure that the reaction continues to completion. In the past, it has been reported that the BCD process was unable to treat high concentration wastes because of salt build-up (CMPS&F, 1997). More recently, however, it has been reported that this problem has been overcome (Vijgen, 2002).

7.2 Off gas treatment:

In addition, BCD plants are equipped with activated carbon traps to minimize releases of volatile organics in gaseous emissions.

In the project in the Czech Republic, not only are the process off-gas streams filtered, but the containment buildings erected around the work area are kept under negative pressure and this air stream is filtered.

Dioxin and OCP values in the air emissions were throughout in the range; 0.001 to 0.01 ng/m³ and 0.0007 to 0.001 mg/m³ respectively.

7.3 Complete elimination:

A balance performed over the total project to date including air exhaust, process gas emissions, treated waste water and back-filled soil showed total elimination of;
Dioxins > 99.99% and OCP's 99.9 to 99.99%

PART II: Criteria on the Adaptation of the Country to the Technology

Note: This part or any present gaps have to be filled in every time the "suitability" of the technology has to be examined for a certain country situation!!

A. Resource needs:

BCD process occupies a relatively small space and so is suitable for deployment near e.g. pesticide stockpiles, provided that the local infrastructure is adequate to support the technology. Some data for the large BCD reactor system of 1000 t/y and oil recovery have been included.

1. Power requirements :

100-125 kWh/h

Energy requirements are relatively low owing to low operating temperatures associated with the BCD process.

The example for the Spolana project is taken: Here is a very reliable E-net available. For emergency back up, a diesel generator is used, namely to be able to shut down the plants safety in the rare event of a power failure.

Requirement: about 60 kWh/h emergency back up for the BCD reactors and 45 kWh/h for the ITD (Indirect Thermal Desorption).

2. Water requirements:

cooling water 10-15 m³/h

3. Fuel volumes:

Fuel gas 40 m³/h

4. Reagents volumes:

a. Hydrogen donor oil, such as No. 6 fuel oil or Sun Par oils No. LW-104, LW-106 and LW-110; → 150-200 t/year

b. Alkali or alkali 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, 1997)

Amounts range from 1 % to about 20 % by weight of the contaminated medium. Here: NaHCO₃ in soil 1-3 %. NaOH: 1.1-1.2 stoichiometric ratio to org. chlorine → for each Cl-atom 1.1 to 1.2 NaOH atoms are needed.

c. Proprietary catalyst amounting to 1 per cent by volume of the hydrogen donor oil: here 0.5 t/year

5. Weather tight buildings:

Building requirements are acc. to project and location.

Process itself has no special requirements other than rain shelter.

7. Sampling requirements/facilities:

9. Laboratory requirements:

Mainly depending on agreements and requirements of the local authorities.

It is also depending upon the target species.

On site requirements:

For PCB's or OCP's (e.g. Lindane, DDT etc.) one can install on-site GC &/or GCMS and so one can do the main QC work. Depending on agreement with authorities this could suffice before we export any materials off-site after treatment, and spot checks by external labs can be made.

For Dioxins for QC one works with a system from USA, using enzymes. Analysis time is perhaps 4 - 6h, but it is still quite expensive and not recognised by authorities. It is useful for internal QC where a local lab for dioxins does not exist.

Requirements in country:

For Dioxin, using a local lab one has a turnaround of 24 h for high resolution.

By recycling the oil now one has much smaller quantities to be exported. Hence waiting time is not a problem. The reactors do not stop to wait for an answer. Only material for off-site disposal needs a regulatory analysis. This is stored in containers until cleared. One can afford to wait for a week, even longer if needed.

In the Czech Rep. **only accredited laboratories are performing the QC analyses.**

11. Number of personnel required:

11.1 Number of Technicians required (skilled labour):

Operator skilled 1 per shift. This operator must be a skilled chemical operator.

11.2 Number of Labourers required (unskilled labour):

1 semi-skilled operator per shift

B. Costs:

BCD (Spolana) status mid 2004: 1400-1700 €/t for org. Chlorine cont 50% for a throughput of 150 t/month.

Operating costs will be € 850-1000/t of pure chemical waste and depreciation € 500/t of chemical waste

1. Installation and commissioning costs [US Dollars]:

2. Site preparation costs [US Dollars or EUROS]:

3. Energy & Telecom installation costs:

4. Monitoring costs:

<p>5. Complying costs:</p> <p>7. Running costs with no waste:</p> <p>9. Decommissioning costs:</p> <p>11. Transport costs of residues: Depending on local situation - should be filled in for the concerning country</p>	<p>6. Reporting costs:</p> <p>8. running costs with waste:</p> <p>10. Landfill costs: Depending on local situation – should be filled in for the concerning country</p>
<p>C. Impact:</p>	
<p>1. Discharges to air: 2-5 m³/h, average 3.5 m³/h. 90% nitrogen and rest H₂</p> <p>3. Discharges to land: Since 2004 is that the process has the choice of using low cost heavy fuel oils or refined paraffinic oils as the donor oil in the process. Heavy fuel oils can be used once only, with the used oil being fed to cement kilns after destruction of POP's. It is now possible to recover and re-use 90-95% of the donor oil which greatly improves the economics of the process and reduces the production of wastes virtually to a solids stream of sodium chloride and carbon from the breakdown of the POP molecule. Discharge to landfill: Salt carbon residue, approx 900-1100t for 1000 t of 50% chlorine pesticides etc.</p>	<p>2. Discharges to water: none</p>
<p>4. Soil impact (noise etc): Treated soil is usually back-filled at site</p>	
<p>D. Risks</p>	
<p>1. Risks of reagents applied: (a) Hydrogen donor oil, such as No. 6 fuel oil or Sun Par oils No. LW-104, LW-106 and LW-110 (b) Alkali or alkali earth metal carbonate, bicarbonate or hydroxide, such as sodium bicarbonate can be handled with normal procedures (c) Proprietary catalyst is non hazardous and is applied in cosmetics. Working with pesticides workers wear Tyvek, gloves contained face mask and breathing filter when handling</p>	
<p>2. Risks of technology: In general the health and safety risks associated with operation of this technology are thought to be low (CMPS&F, 1997, Rahuman et al., 2000 in annex IV, References) although a BCD plant in Melbourne, Australia, was rendered inoperable following a fire in 1995. The fire is thought to have resulted from the operation of a storage vessel without a nitrogen blanket (CMPS&F, 1997). Some associated pre-treatments such as alkaline pre-treatment of capacitors and solvent extraction have significant fire and explosion risks, although they can be minimized through the application of appropriate precautions.(Ibid) At the present stage the risk of fire is very limited as only at one point in the process is oil above flash point in a pressure vessel under N₂ atmosphere.</p>	
<p>3. Operational risks: Feed to plant is automatic. Plant comes fully constructed with control unit. All skids for large plants are conform EU road transport limits. Processing is easy as operation follows with fixed recipes. Heating and pressure control are fully automatic and intrinsically safe</p>	
<p>E. Constructability:</p>	
<p>1. Ease of installation/construction of plant: Processing is easy as operation follows with fixed recipes. Heating and pressure control are fully automatic and intrinsically safe</p> <p>3. Ease of operation: See under 1</p>	<p>2. Ease of shipping/transit: Virtually all containerized sizes.</p> <p>4. Ease of processing :</p>
<p>F. Output/generation waste</p>	
<p>1. Generated waste (% of input waste) Spolana Case: for a site remediation job with an input of 35,000 t 450 t of waste will be produced either from the BCD process or material BCD cannot treat, that is less than 1.5%</p>	<p>2. Deposited waste at landfill (% of input waste) For treatment of chemicals, pesticide wastes PCB's; with about 50% organic chlorine one cannot avoid producing about 1.5 times the input of chemicals. However this material is POP's and hydrocarbons free and can be deposited in low cost landfill. pH is high due to excess NaOH. OCP's etc. are below analytical detection. Any other process claiming differently is ignoring the fact that the carbon is then going to the atmosphere and salt going away in large volumes of dilution water.</p>

3. Waste quality properties (pH, TCLP)

**Note: This Technology Specification and Data Sheet (TSDS) does not certify any particular technology, but tries to summarise the state of the art of the concerned technology on the basis of data delivered by the companies or other sources, which have been made available to the author and refers the reader to original documents for further evaluation. Without the efforts below listed technology suppliers it would not have been possible to set up this TSDS. Date: 01.09.2009*

Technology suppliers that have contributed to this TSDS:

BCD International, Inc., United States
Thermal and Chemical Soil Remediation Ltd (TCSR), Czech Republic
BCD Technologies Pty Ltd, Australia
S.D. Myers de Mexico

References:

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