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Disposal in Ukraine, Belarus, Kazakhstan and Armenia

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List of Proved Destruction Technologies of POPs and ODS's

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Contents

Abbreviations and acronyms

BAT	Best Available Techniques
BCD	Base-Catalysed Decomposition
BDE	Brominated Diphenyl Ether
BEP	Best Environmental Practices
CEIT	Country with Economies in Transition
CFCs	Chlorofluorocarbons
CKD	Cement Kiln Dusts
DDT	1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (dichlorodiphenyltrichloroethane)
DE	Destruction Efficiency
DRE	Destruction Removal Efficiency
ESM	Environmentally Sound Management
EPS	Expanded Polystyrene Insulation
EU	European Union
FGC	Flue Gas Clean-up
GEF	Global Environment Facility
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
GPCR	Gas-Phase Chemical Reduction
HASP	Health And Safety Plan
HBB	Hexabromobiphenyl
HBCD	Hexabromocyclododecane
HCB	Hexachlorobenzene
HCBD	Hexachlorobutadiene
HCH	Hexachlorocyclohexane
HFC	Hydrofluorocarbons
IBC	Intermediate Bulk Container
ISO	International Organization For Standardization
LHV	Lower Heating Value
MSW	Municipal Solid Waste
ODS	Ozone-Depleting Substances
PAH	Polycyclic Aromatic Hydrocarbon
PBB	Polybrominated Biphenyl
PCB	Polychlorinated Biphenyl

PCDD	Polychlorinated Dibenzo-*p*-Dioxin
PCDF	Polychlorinated Dibenzo-Furan
PCN	Polychlorinated Naphthalenes
PCP	Pentachlorophenol
PCT	Polychlorinated Terphenyl
PFOS	Perfluorooctane Sulfonic Acid
POP	Persistent Organic Pollutant
PTS	Persistent Toxic Substances
QA	Quality Assurance
QC	Quality Control
RDF	Refuse-Derived Fuel
SCWO	Supercritical Water Oxidation
SOP	Standard Operational Procedure
TCB	Trichlorobenzene
TCLP	Toxicity Leach Test Procedure
TEAP	Technology And Economic Assessment Panel
TEQ	Toxicity Equivalence
TRBP	Thermal reduction batch processors
TSCA	Toxic Substances Control Act
UNECE	United Nations Economic Commission for Europe
UNIDO	United Nations Industrial Development Organization
UNEP	United Nations Environment Programme (actual UN Environment)
VOC	Volatile organic compounds
WHO	World Health Organization
XPS	Extruded Polystyrene Insulation
XRF	X-ray fluorescence

Available and applicable technologies for the disposal of POPs

The concept of a facility dedicated to the management of waste is not new. Long before the enactment of waste legislation (hazardous or non-hazardous), companies which produced waste already recognized the need for the specialized treatment and disposal of their wastes. Many waste producers constructed and operated their own dedicated facilities, typically onsite facilities.

Other companies that generated waste and did not have a suitable site or did not generate a sufficiently large volume of waste to justify the investment in an on-site facility transported their waste off site to specialized facilities for treatment and disposal. Such facilities are typically referred to as commercial, off-site facilities. The commercial waste management industry in Western Europe thus began the development of these off-site facilities in the late 1960s[1]. Their role was to collect and transport waste to specialized off-site facilities where they carried out the treatment and disposal of that waste. It is important to note that today the waste industry is organized on the subregional level, i.e. not every country has developed a full-blown waste management industry, but services are shared between countries.

Just as there are many types of waste, there are many ways in which wastes can be managed. A waste facility may function with just one technology, or it may combine multiple technologies, particularly if it is a commercial facility serving a number of domestic and foreign waste producers.

Selection and Qualification of a Disposal Technology Including Management of By-Products and Residuals

Environmental Performance: POPs destruction technologies should be evaluated on the level of achieved destruction and irreversible transformation. This requires consideration of all waste output streams from the technology, including POPs other than those being destroyed that may be unintentionally produced during the destruction process (dioxins, furans).

Destruction efficiency[2] (DE) is the percentage of originating POPs destroyed or irreversibly transformed by a particular method or technology. Destruction removal efficiency[3] (DRE) only considers emissions to air and is the percentage of original POPs irreversibly transformed and removed from gaseous emissions.

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[1] European Commission's Joint Research Centre, 2018, Best Available Techniques (BAT) Reference Document for Waste Treatment (BREF)

[2] Calculated on the basis of the mass of the POP content within the waste, minus the mass of the remaining POP content in the gaseous, liquid and solid residues, divided by the mass of the POP content within the waste, i.e., DE = (POP content within waste – POP content within gas, liquid and solid residual) / POP content within the waste.

[3] Calculated on the basis of the mass of the POP content within the waste, minus the mass of the remaining POP content in the gaseous residues (stack emissions), divided by the mass of the POP content within the wastes, i.e., DRE = (POP content within waste – POP content within gas residual) / POP content within the waste.

The provisional definition set up below recognizes the following[4]:

a) Both DE and DRE are a function of the initial POP content and do not cover any fraction of other unintentionally produced POPs during destruction or irreversible transformation;
b) DE is an important criterion to assess technology performance for destruction and irreversible transformation, but can be difficult to measure in a reproducible and comparable manner;
c) BAT and BEP are available in order to ensure the anticipated environmental performance is achieved, including expected DE; and
d) Pertinent national legislation, international rules, standards and guidelines apply to these operations (For example, in Japan, the Ministry of the Environment in 2010 issued a "Technical Guideline for the Environmentally Sound Treatment of PFOS Wastes", which states that destruction levels for PFOS and its salts must be over 99.999 per cent).

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 ng TEQ/Nm[5]
    ii. All other POPs: pertinent national legislation and international rules, standards and guidelines, (examples of pertinent national legislation can be found in annex II of General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (UNEP, 2017));
b) Aqueous release: pertinent national legislation and international rules, standards and guidelines (for example in Japan is Water Pollution Control Law, which contains emission standards for effluent containing PCBs; in US is 40 CFR 268.48 Universal Treatment Standards for Hazardous Wastes, which contains standards for the treatment of hazardous waste prior to land disposal and aqueous waste prior to release;
c) Solid residues: POP contents should be below the 50ppm Stockholm Convention Low POPs limit[6]. However, if the POP content is above the low POP content, the solid residues should be treated.

In addition, technologies for destruction and irreversible transformation should be operated in accordance with BAT and BEP.

DE and DRE should be used together to demonstrate a level of destruction and irreversible transformation, however, as neither DE nor DRE take into account the potential transformation

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[4] UNEP, 2017, General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants

[5] TEQ (Toxic Equivalent) as referred to in Annex C, part IV, paragraph 2, to the Stockholm Convention, but only for PCDDs and PCDFs. Nm^3 (normal cubic meter) refers to dry gas, 101.3 kPa and 273.15 K. Standardization at 11 percent O_2. Standardization at 10 percent O_2 for cement kilns co-incineration.

[6] Note that this value is well above the human health screening level, so health protection measures need to be taken when working with POPs-contaminated solid residues even below 50 ppm.

of the original POP to an unintentionally produced POP, potential releases of unintentionally produced POPs have to be considered too when choosing a particular operation.

Safeguard Measures. These include documented processes, procedures and oversight actions that should be part of a monitoring and evaluation plan, including:

- Institutional/regulatory commitment and capacity to undertake appropriate oversight and enforcement;
- A national POPs inventory and endorsed NIP, regularly maintained and updated consistent with Convention obligations;
- Unambiguous legal custody and ownership of POPs stockpiles and wastes, covering rights of access, assignment of financial liability for disposal and environmental damage, and monitoring and site closure;
- Credible environmental assessment and permitting applied to facilities and activities and benchmarked against international standards and practice;
- Performance monitoring during operations and documentation of the fate of all residues;
- Public participation, consultation and disclosure[7] including timely access to information about POPs stockpile and waste disposal and input on how these activities are conducted;
- Health, safety and emergency response plans covering protection and monitoring of workers involved in operating the technology and any potentially exposed members of the public.

Commercial Viability and Economies of Scale. Successful, sustainable performance of any technology also depends upon commercial or financial sustainability. In general, projects should employ the most cost effective commercial arrangement that also serves to maximize the quantity of POPs disposed of, and net global environmental benefit at minimum risk to completion. These conditions are most often satisfied where the selected technologies are packaged on a complete turn-key basis operating at a predictable “all inclusive” unit cost, with appropriate performance guarantees, free of any dispute over technology ownership or licensee rights. This generally requires that a vendor possess the rights to the technology, a demonstrated track record, and the capacity to operate it at the required location. It also includes technical support and training capacity, and the financial strength to undertake the proposed work, particularly where 1) the application is to occur in developing countries and CEITs (Country with Economies in Transition) and 2) technology transfer is involved. Where the vendor arrangements involve local partnerships, national government guarantees may be required to ensure the sustainability of local arrangements and completion of the disposal works. However, while this approach provides large assurance that the work is done in compliance with best international practices, it limits the build-up of national capacity to handle wastes in a national system in the longer term.

The need for disposal capacity, current and future, and the potential for economies of scale can influence POPs destruction technology choices. That need also guides decisions regarding

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[7] UNECE, 1998, Aarhus Convention

development of domestic capacity vs. utilization of qualified facilities elsewhere. In many cases, countries should consider combining their disposal requirements with others and cooperating in regional pre-treatment and disposal capability.

They may also consider integrating POPs stockpile and waste disposal with development of more broadly-based hazardous and chemical waste management infrastructure so as to maximize the effectiveness of scarce financial resources. Focusing disposal capacity only on POPs wastes will lead to uneconomic decisions, as the POPs volumes are relatively small compared to the overall hazardous wastes volumes every country has to deal with.

Infrastructure considerations. Most qualified POPs disposal technologies have been implemented in developed countries possessing mature regulatory and institutional frameworks, good supporting infrastructure (water, energy, analytical labs, etc.), a strong technical expertise base, and sufficient resources to support their application.

However, these supporting attributes may not be as readily available in developing countries and CEITs. High-performance technologies involve complex equipment, sophisticated controls and processes and require such things as reliable power and other utilities for safe and sustainable operation.

A technology selection process has to assess these infrastructure needs and prudently balance the decision between technological complexity and practical applicability vs. simplicity of operation.

Recommendation:

- Technical and environmental qualification of POPs disposal technology should be destruction performance-based.
- The evaluation of safeguards provisions and commercial viability should also be included in the selection process.
- Developing countries and CEITs should not be held to higher standards than those accepted in developed countries.
- Disposal is only part of the POPs management process and must be integrated with additional steps involving capture, containment, secure storage, pre-treatment, transport, and post disposal residuals management/monitoring.
- Economies of scale should be considered in any decision to build new or use existing facilities.
- Integration of POPs disposal requirements with those required for environmentally sound chemical/hazardous waste management should likewise be considered as part of broader national or regional infrastructure development.
- Inventories of POPs stockpiles and waste subject to disposal should be prioritized in terms of POPs concentration and risk of release.
- Environmentally sound disposal of POPs is not generally limited by availability of suitable technology.
- Primary Environmental Performance requirements recommended are:
    - Current Basel and Stockholm Guidelines should apply.
    - As a general principle, levels of POPs destruction and irreversible transformation should consider all POPs in waste output streams of a technology.
    - POPs destruction efficiency (DE) applicable to the originating POPs should be >99.99% with Destruction Removal Efficiency (DRE) >99.9999% as a supplemental requirement, particularly in relation to POPs release to air.

  - Low POPs content as specified in the current Basel Guidelines should apply as an upper limit for residuals.
  - Unintended release limits should be set at nominal developed country standards; i.e. 0.1 ng TEQ/Nm3 for PCDD/PCDF air emissions.
- Specification of BAT/BEP for design and operating conditions should be formulated on a technology-specific basis, where practical. While the highest overall destruction efficiency possible is preferable, where large amounts of POPs require disposal and financial capacity is limited, the actual volume of POPs eliminated and associated global environmental benefit may be maximized by use of a lower cost option that achieves the minimum DE, rather than a higher cost option that greatly exceeds the minimum DE.
- Safeguard measures are needed to assure implementation and achievement of performance as specified:
  - Institutional/regulatory commitment and capacity for oversight and enforcement.
  - Linkage to a national POPs inventory and endorsed NIP, regularly maintained and updated.
  - Undisputed legal custody and ownership of stockpiles and wastes with attendant financial responsibility.
  - Credible environmental assessment and permitting process.
  - Environmental performance demonstration.
  - Provision for operational monitoring of performance and tracking of POPs from acquisition to final disposition.
  - Public participation, consultation and disclosure.
  - Health, safety and emergency response plans.
- An evaluation of commercial viability and sustainability should be applied in the selection of POPs disposal technology including consideration of:
  - Availability of the commercial offering at predictable and competitive cost, inclusive of set up, pre-treatment, training and operational supervision, including appropriate performance guarantees.
  - Technology maturity in the market place.
  - Technology ownership or licensee rights.
  - Capacity of vendor/operator in terms of relevant track record, technical support capacity and financial strength to undertake the proposed work.
  - Local partner capability, including relevant technical/operational experience and financial capacity, as applicable.
  - Backstopping in the form of completion guarantees, as applicable.

Installations for the treatment of waste containing POPs

Waste transfer installations

Operations carried out in these installations include: reception, bulking, sorting, intermediate storage prior to submission to a disposal/recovery operation. In some cases, blending and mixing may also be carried out in these installations to optimize the properties of the wastes to be disposed of. Waste transfer stations may involve individual operations or may be an integrated part of a treatment process. All sites typically undertake some kind of bulking operation to agglomerate the solids, where liquids are decanted from one container to another. Bulk volumes of liquid can be transferred from a tanker to a holding tank, small volumes from fractions of liter up to a more than 200 liter in sealed drums. Operations typically carried out are inspection, sampling, physical sorting and packaging, decanting, blending, drum emptying, storage, drum/IBC reclamation and in some cases disposal of wiping cloths, solidification and the crushing of oil filters. Waste transfer stations tend to fall into two categories according to the objective of the installation[8]:

- **Focus on the output stream.** This corresponds to sites that act as a feeder for other processes: e.g. solvent regeneration, incineration, chemical treatment. These sites target specific waste streams that can be checked, analyzed and bulked to provide a steady feedstock for an associated process. They may also take in and process a variety of other materials in order to provide a full service to their clients. These sites tend to handle a much higher proportion of certain waste streams and acceptance, storage and control systems are therefore designed for these wastes.
- **Focus on the input waste.** These sites are independent transfer stations and generally accept a full range of materials from the neighboring area. Typically they also bulk and blend materials to produce a range of waste streams suitable for disposal through different treatment, recovery and disposal processes, but they do not usually target any specific waste group. There may be a bias towards particular waste streams, but this will likely be due to local patterns of waste arising and commercial opportunities, rather than the need to provide a feedstock for a particular downstream process.

The majority of operations linked to waste preparation may be distinguished in two groups:

- **Regrouping/Reconditioning.** Here the aim is to group together wastes in small or medium quantities, when they have the same nature and when they are compatible (e.g. exclude risks of spontaneous ignition). The resulting waste still has to be treated though. The purpose of regrouping is to obtain larger and more homogeneous volumes for waste treatment, to improve safety (e.g. facilitation of handling) and to rationalize the logistics cost. The combination of processes used in waste preparation and in pretreatment operations depends on the specifications of final treatment.
- **Pretreatment.** Here the aim is to adapt the waste to the type of recovery and/or disposal of the final treatment available. Pretreatment covers several aspects. It can be defined as those operations that lead to homogenization of the chemical composition and/or physical characteristics of the wastes in order to better control then the disposal process. Pretreatment produces a waste, which may be very different from the initial waste, although not from a regulatory point of view. This pretreated waste still has to be treated in a recovery and/or disposal plant. At the end of the pretreatment process, the pretreated waste should comply with chemical and physical specifications that are fixed by the end users.

Grouping and pretreatment activities may be located at the same site as the final treatment, on the waste production site or on a particular dedicated site. Nevertheless, regardless of the location, the operating processes are the same.

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[8] See *European Commission's Joint Research Centre, 2018*

The following disposal operations, as provided for in Annex IV, sections A and B, of the Basel Convention, should be permitted for the purpose of destruction and irreversible transformation of the POP content in wastes when applied in such a way as to ensure that the remaining wastes and releases do not exhibit the characteristics of POPs[9]:

(a) D9: Physico-chemical treatment;

(b) D10: Incineration on land;

(c) R1: Use as a fuel (other than in direct incineration) or other means to generate energy; and

(d) R4: Recycling/reclamation of metals and metal compounds, but restricted to activities of primary and secondary metallurgy.

POPs that are isolated from a waste stream during pre-treatment should subsequently be disposed of in accordance with operations D9 and D10.

It should be noted that pertinent national legislation apply to these operations and that the operations should be used in accordance with the BAT and BEP standards developed under the Stockholm Convention, as presented in the *Guidelines on best available techniques and provisional guidance on best environmental practices relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants*[10]. Consequences of not conducting the operations according to the standards outlined in the BAT and BEP guidance can lead to the formation and release of POPs into the environment.

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[9] See *UNEP, 2017*

[10] UNEP, 2007, Guidelines on best available techniques and guidance on best environmental practices

Characteristics of Potentially Applicable POPs Disposal Technologies (Destruction/Irreversible Transformation)[11],[12],[13]

Technology	Application	Indicative Cost	Pre/Post Treatment Requirements	HBB/ HBCD/ HCBD	PCB	PCDDs/ PCDFs	PCN	PCP	Pesticides POPs	PFOS	POP-BDEs	Reported DE %	Reported DRE %	Residue POPs Release	State of Commercialization/ Adaption
1.Base-catalyzed decomposition (BCD)	PCBs, POPs pesticides, PCDD in soil, solid, sludge and liquids	• US$0.7-2.2/kg depending on waste • US$300/m3 (Soil) • 1.4-1.7 Euro/ kg. (2004)	• pH adjustment • Moisture control • Size segregation/ reduction • Thermal desorption step prior to treatment. • ESM disposal of treated material required. • Chemical additions (sodium hydroxide)	ND*	Yes	Yes	ND	Yes	Yes, for certain pesticides: chlordane, HCH, DDT, HCB	ND	ND	99.99-99.9999	>99.9999	• <2 mg/kg HCB/lindane in soil • <3 mg/kg PCCD in soil • <60 mg/kg PCCD in demolition waste	• Commercially available through established technology vendor/ licensee arrangements. • Several facilities operating worldwide. • Suitable for establishment in many countries provided volumes justify supporting high capital cost infrastructure. • Moderate to high complexity.
2.Gas Phase Chemical Reduction (GPCR)	PCBs, POPs pesticides, PCDD in spoil, solid, sludge and liquids.	• US$0.4-2.0/ kg (based on operating cost) • Capital cost US$5-10 million depending on mobile or fixed	• For solids requires thermal desorption separation prior to treatment.	Yes	Yes	Yes	Yes	Yes	Yes for all pesticides	Yes	Yes	>99.9999	>99.9999	• No residual POPs content or releases noted.	• Demonstrated in pilot and small commercial facilities in developed countries. • Fixed and mobile configurations available. • Require secure infrastructure, trained technical staff, laboratory support, utilities and re-agent supply. • High level of complexity including safe handling of hydrogen.
3.Plasma Arc	PCBs, POPs pesticides, PCDD in soil, solid, sludge and liquids	• US$0.5 to 3.0/ kg • US$1.0-1.5 million for 150 kW unit	• For solids requires thermal desorption separation prior to treatment. • ESM disposal of treated material required.	ND	Yes	ND	ND	ND	Yes, for most pesticides, including chlordane, chlordecone, DDT, endosulfan, heptaclor	ND	ND	>99.9999	n/a	• <0.5 mg/l POPs liquid in effluent • <1 ng/ m3 POPs in air • <0.1 ng PCDD TEQ/Nm3 • Solidified residuals generally meet leachate limits	• Commercially available technology with a number of operating facilities in developed countries. • Technology vendors with stable licensee arrangements capable of competitive tendering worldwide. • Fixed and mobile facilities potentially available. • Require secure infrastructure, trained technical staff, laboratory support and utilities and reagent supply. • High level of complexity
4.Pyrolysis/ Gasification	PCBs, POPs pesticides, PCDD in soil, solid, sludge and liquids (in principle)	• US$0.75 – 1.00/kg (Based on operating costs) • US$275-500/ m3 (Soils)	• Low moisture content required - drying • ESM disposal of treated material required. • High energy costs	ND	Yes	Yes	ND	ND	Yes	ND	ND	99.974	99.9999	Claimed to meet US/EU emission and disposal limits	• Commercial units from a number of technology vendors but limited application to POPs wastes. • Subject to demonstration of stable licensee arrangements should be capable of competitive tendering worldwide. • Fixed and mobile facilities potentially available. • Require secure infrastructure, trained technical staff, laboratory support and utilities and re-agent supply. • High level of complexity. • Moderate power consumption with reliable water and electrical supply

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[11] See *GEF, 2011, Selection of Persistent Organic Pollutant Disposal Technology for the Global Environment Facility A STAP advisory document*

[12] See *UNEP, 2017*

[13] European Commission, 2018, Best Available Techniques (BAT) Reference Document for Waste Incineration

5.GeoMelt™	PCBs, POPs pesticides, PCDD contaminated soils or granulated solids	US$200-500/ m3 (soils)	• Batch mixing. • Dewatering/drying • Off gas emission control required • ESM disposal of treated material required.	ND	Yes	Yes	ND	ND	Yes	ND	ND	90 to 99.99	99.99-99.9999 (with off gas treatment)	• Negligible air emission claimed. • Solidified residuals generally meet leachate limits	• Commercial operating facilities in a number of developed countries. • Require secure infrastructure, trained technical staff, laboratory support and utilities and reagent supply. • Technology vendor with stable licensee arrangements capable of competitive tendering worldwide. • High power consumption. • High level of complexity.
6.Supercritical water oxidation (SCWO)	• PCBs, Chlordane, PCDD, PCDF. • Liquid and slurries with <20% organic content, and particle size under 200um • Vendor reports capability for 100% organic content	Capital costs US$1.2-1.5 million	Waste preparation to meet feed requirements.	ND	Yes	Yes, for PCDDs	ND	ND	Yes, for certain pesticides: chlordane and DDT	ND	ND	98.7-99.8 Vendor re-ports higher DE potential	>99.9999	Requires assessment	• Specialized commercial plants operating in a number of developed countries. • Mobile plant in shipping containers available. • Remains under evaluation and demonstration for more general POPs applications. • Technology vendor with stable licensee arrangements that should be capable of competitive tendering worldwide. • High level of complexity
7.Cement Kiln Co-disposal	PCBs and POPs pesticide wastes in liquid and solid form	• US$1.0-5.0/kg • Facility specific.	• Specialized size reduction and injection measures. • Blending to meet chlorine content limitations on process	Yes	Yes	Yes	Yes	Yes	Yes, for all pesticides	Yes	Yes	<99.9999	<99.9999	Air emissions <0.1 ng PCDD-l/m3	• Commercial application in developed countries and demonstrations in developing countries. • Generally limited to relatively modern rotary kiln units with overall BAT/BEP environmental performance equipped with appropriate POPs waste handling/ injection infrastructure as well as monitoring capacity. • Application requires case by case assessment and performance demonstration.
8. Hazardous waste incineration	All POPs wastes in any physical form	US$ 0.1-2.5/kg depending on waste type and form	• Depending on facility, size reduction, dewatering, and waste blending. • ESM residue disposal capacity required.	Yes	Yes	Yes	Yes	Yes	Yes, for all pesticides	Yes	Yes	99.88- 99.999	99.9999	• Air emissions <0.1 ng PCDD-l/m3 • Low discharges to water effluent. • 1,500 ng PCDD TEQ/ kg for APC residues. • 50 ng PCDD TEQ/kg ash.	• Extensive commercial application on developed countries. • High capital and operating costs. • Sophisticated emission controls and monitoring required. • Economies of scale >30,000 t/ year generally required for development with broad application to hazardous organic wastes generally. • Mobile/semi-mobile 2-5,000 t/year capacity available but with cost premium and potential environmental performance penalties.

* ND stands for “not determined” and indicates that information is not available to confirm the use of the technology for certain POPs.

1. Base-catalysed decomposition (BCD)[14],[15]

BCD has been used at two commercial operations within Australia, with one 25 years old facility still operating. Approx. 8-10,000 tonnes of low-concentration PCBs and PCBs contaminated oils, 25 tonnes of pesticide chemicals and pesticide waste, 15 tonnes of pesticide concentrates collected from soil remediation. Another commercial system has been operating in Mexico (from 1998 until today treated 1,400 tonnes of liquids and solids with low-concentration PCBs. 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 now under full scale construction within the Czech Republic. The plant will treat 35,000 tonnes of soil and building rubble contaminated with PCDD/F, HCB and HCH. In addition to treating more than 1,000 tonnes of contaminated concentrate from the first stage thermal desorption process more than 200 tonnes of waste pesticide intermediates will also be treated.

BCD has been successfully applied in the 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 3,500 tonnes of pure HCH waste has been destructed to TCB (trichlorobenzene), which was used by the industry. In the US, a BCD system has been successfully applied in combination with thermal desorption at the beginning of the 90s. In Japan, a continuous process for oils with low contamination of PCBs has been developed.

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

Process description: Based on patents developed at the Cincinnati Risk Reduction Research Laboratory by C. Rogers, A. Kornel and their group from the US EPA, licenses have been given to various vendors. Initially, the technology was developed for the destruction of halogenated compounds. With 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 gravity or centrifugation. The oil and catalyst may be recovered for reuse in other 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

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[14] See UNEP, 2017

[15] UNEP, 2002, Vijgen J. McDowall Ir. Ron, Auckland New Zealand for Secretariat of the Basel Convention, **“**Destruction And Decontamination Technologies For PCBs And Other POPs Wastes Under The Basel Convention, A Training Manual For Hazardous Waste Project Managers” (Vol.C-Annexes)

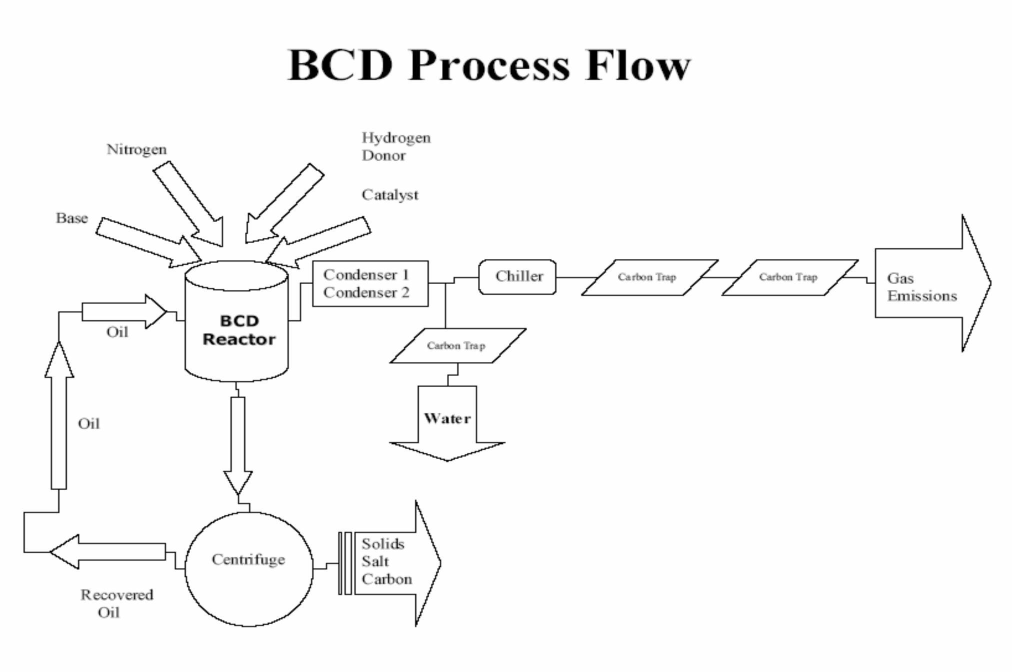
heteroatoms attached and can be disposed of as any non-toxic material. The BCD process has the advantages of not requiring very high temperatures, high pressure, or energetic reagents.

When pesticides or other pollutants are contaminants in soil, sediment or other solid matrices, the BCD process is usually linked with a pre-treatment step such as thermodesorption to remove the contaminant from the matrix and collect it. The collected contaminants can be destroyed on-site in a mobile BCD vessel designed to treat liquids.

In 1997, the BCD inventors C. Rogers and A. Kornel discovered a new more effective BCD catalyst while working as visiting scientists at the US EPA 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. With the newly discovered BCD catalyst, PCBs in 20% concentrations are destroyed within 20-30 minutes and 30% PCBs concentrations are destroyed within 60-90 minutes.

In 2004, during a trial at the pilot plant at the Spolana site in the Czech Republic, HCB waste with an organic chlorine content of 55% and dioxins in dust up to a level of 1,620,000 ng/kg I-TEQ have been successfully destroyed.

Process diagram:



Efficiency: DEs of 99.99–99.9999 per cent have been reported for DDT, HCB, PCBs, PCDDs and PCDFs, HCH and PCP. DEs greater than 99.999 per cent and DREs greater than 99.9999 per cent have also been reported for chlordane and HCH. It has also been reported that reduction of chlorinated organic to less than 2 mg/kg is achievable.

Latest results of the pilot-scale demonstration at Spolana[16] show that 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. The conclusions of the tests in Spolana have been formulated as follows: "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."

Waste types: BCD should be applicable to other POPs in addition to DDT, PCBs, PCDDs and PCDFs, HCH and Lindane wastes, HCB, PCP and other chlorinated phenols. BCD should be capable of treating wastes with a high POPs concentration, with demonstrated applicability to wastes with a PCB content of above 30 per cent by weight. The process is not selective, all organically bonded halogen groups are attacked and degraded.

Direct treatment of capacitors is not possible and solvent extraction is required first.

Some facilities shred the capacitors and treat the material with sodium hydroxide. The shredded material can be treated with the BCD process. Although there have been reports that the formation of salt within the treated mixture could limit the concentration of halogenated material that could be treated with BCD, more recent reports suggest that this problem has been overcome.

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 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, as is the case with pesticides, they should be removed by distillation prior to treatment.

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[16] See *UNEP, 2002*

Emissions and residues: 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 temperatures as low as 150 °C. It should be mentioned that in the Olympic site project in Australia chlorophenols and PCDD/F were treated at the same time. PCDD/Fs 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, refer to the literature produced by BCD Group Inc.

Release control and post-treatment: Depending on the type of hydrogen-donor oil used, the slurry residue may be treated in different ways. If No. 6 fuel oil has been used, the sludge may be disposed of as a fuel in a cement kiln. If more refined oils are used, these may be removed from the sludge by gravity or centrifuge separation. The oils can then be reused and the remaining sludge can be further treated for use as a neutralizing agent, or disposed of in a landfill. In addition, BCD facilities are equipped with activated carbon traps to minimize releases of volatile organic compounds in gaseous emissions.

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 POPs. Where refined paraffinic oils are 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.

Energy requirements: 100-125 kWh/h. Energy requirements are relatively low owing to the low operating temperatures associated with the BCD process. In Spolana, the facility is connected to the electrical grid. For emergency backup, a diesel generator is used, namely to be able to shut down the plant in a safe way in the rare event of a power failure. Requirement: about 60 kWh/h emergency backup for the BCD reactors and 45 kWh/h for the ITD (Indirect Thermal Desorption).

Material requirements:

- Water requirements: cooling water 10-15 m^3/h;
- Fuel volumes: Fuel gas 40 m^3/h;
- 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 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. Amounts range from 1 % to about 20 % by weight of the contaminated medium. Here: $NaHCO_3$ in soil 1-3 %. NaOH: 1.1-1.2 stochiometric ratio to org. chlorine for each Cl-atom 1.1 to 1.2 NaOH atoms are needed;
    - (c) Proprietary catalyst amounting to 1 % by volume of the hydrogen donor oil: here 0.5 t/year.

On site requirements: For PCBs or OCPs (e.g. Lindane, DDT etc.) one can install on-site GC and/or GCMS and so one can do the main QC work. Depending on the agreement with authorities this could suffice before any materials are exported off-site after treatment, and spot checks by external labs can be made. For dioxins, QC works with an enzyme-based system from the US. Analysis time is approx. 4 - 6h, but the process is quite expensive and not recognized by authorities. However, it is useful for internal QC where a local lab for dioxins does not exist.

Portability: Modular, transportable and fixed facilities have been built.

Health and safety: In general, the health and safety risks associated with operation of this technology are thought to be low, although a BCD facility 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. Some associated pre-treatments such as alkaline pre-treatment of capacitors and solvent extraction present significant risks of fire and explosions, but those risks can be minimized through the application of appropriate precautions.

Capacity: BCD can process up to 9.5 m^3 of waste per batch and can treat two to four batches per day. The BCD process occupies a relatively small space and such is suitable for deployment near e.g. pesticide stockpiles, provided that the local infrastructure is adequate to support the technology. Some data for a large BCD reactor system of 1000 t/year and oil recovery have been included in following.

Costs: BCD (Spolana) status mid 2004: 1,400-1,700 €/t for org. chlorine content of 50 % and a throughput of 150 t/month. Operating costs will be € 850-1,200/t of pure chemical waste and depreciation € 500/t of chemical waste.

Other practical issues: 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 lower-chlorinated congeners are more toxic than higher-chlorinated congeners. It is therefore important that the process be appropriately monitored to ensure that the reaction reaches completion. In the past, it was reported that the BCD process was unable to treat high-concentration wastes because of salt build-up. However, it has been reported that this problem has been overcome.

State of commercialization: BCD has been used at two commercial operations in Australia, one of which is still operating. Another commercial system has been operating in Mexico since 1999. In addition, BCD systems have been used in projects in Australia, Czech Republic, Spain, and the United States of America.

Summary:

- Commercially available through established technology vendor/ licensee arrangements.
- Several facilities operating worldwide.
- Suitable for establishment in many countries provided volumes justify supporting high capital cost infrastructure.
- Moderate to high complexity.

2. Gas-phase chemical reduction (GPCR)[17]

A commercial GPCR system operated in Australia for more than 5 years, treating more than 2,500 tonnes of PCBs, DDT and other POPs. In 1999, a full-scale test on HCB was conducted using the commercial plant.

GPCR technology licensees in Japan have built and operated a semi-mobile GPCR plant for the treatment of PCB wastes. The technology was also tested in the US as part of the ACWA (Assembled Chemical Weapons Assessment) Program for the destruction of chemical warfare agents. Through this testing the GPCR technology was proven to be effective for treatment of chemical warfare agents.

The GPCR technology can be used in conjunction with thermal desorption technologies for treatment of soil and sediment at rates of up to 10 tonnes per hour.

The GPCR technology was selected by UNIDO for a pilot project for treatment of up to 6,000 tonnes of PCB wastes in the Slovak Republic.

Additional approvals received:

-for PCB and dioxin waste in Japan

-for PCBs TSCA permit in USA

-for PCBs and other toxic compounds in the Province of Ontario (Canada)

Process description: The GPCR process involves the thermochemical reduction of organic compounds. 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: a front-end system (where the contaminants are transformed into a suitable form for destruction in the reactor), a reactor (which reduces the contaminants, at this stage in gas phase, using hydrogen and steam), and a gas scrubbing and compression system.

The front-end units will differ depending on the waste matrix. For example, bulk solids such as drummed chemicals, electrical equipment, spent carbon, etc. are placed into a Thermal Reduction Batch Processor (TRBP), which desorbs the contaminants from the solid material, and then conveys them to the reactor for destruction. Watery wastes and high-strength oily wastes are injected into a preheater that vaporises the liquids in an indirectly fired heat exchanger. The gases are mixed with hydrogen and steam to a temperature of 600°C prior to introduction to the GPCR reactor.

In the case of soil and sediment treatment, contaminants are first desorbed from the solids using a thermal desorption device (of which there are many proven systems available worldwide). The gas containing the contaminants is then condensed, the water removed, and the remaining

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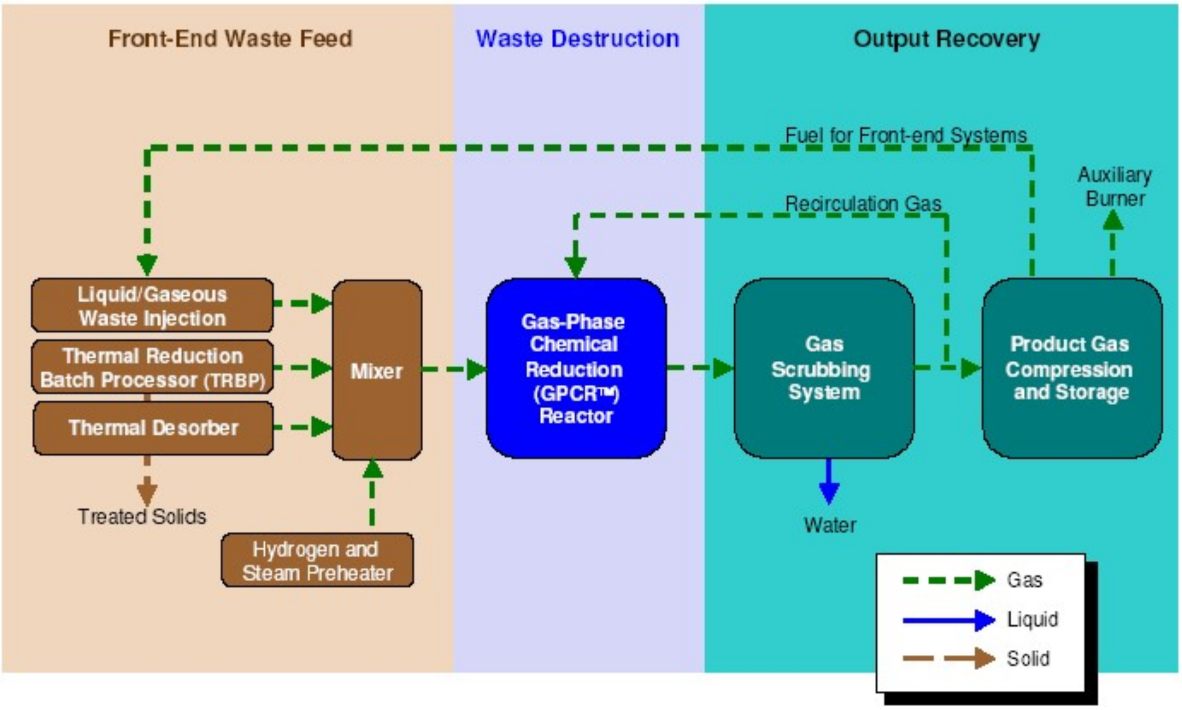
[17] See UNEP, 2017, UNEP, 2002

concentrated contaminant liquid fed to the preheater and GPCR reactor as a contaminant concentrated liquid waste feed.

Process diagram: Block Flow Schematic:



Efficiency: DEs of 99.9999 per cent have been reported for DDT, HCB, PCBs, PCDDs and PCDFs.

Commercially the system operated more than 5 years at Kwinana in Western Australia, treating PCBs, HCBs and DDT. Here efficiencies of at least 99.9999% were demonstrated. In commercial-scale performance tests in Canada, the gas-phase reduction process achieved DE and Destruction and Removal Efficiencies (DRE) with high-strength PCB oils and chlorobenzenes. Dioxins that were present as contaminants in the PCB oil were destroyed with efficiencies ranging from 99.999 to 99.9999%.

Engineering testing on batches of 3, 9 and 27 drums (205 liter size) of HCB wastes showed that, "Results of the trials indicated that the system effectively desorbed approximately 98% of the waste input to the Thermal reduction batch processors (TRBP). In excess of 99.9999%of the HCB and chlorobenzene present in the waste was volatilized in the TRBP and swept to the reactor for destruction."

Waste types: GPCR is expected to be able to treat all POP wastes, including aqueous and oily liquids, soils, sediments, sludges, transformers and capacitors. The GPCR technology has treated HCBs and PCBs and DDT, other chlorinated pesticides and POPs related wastes such as dioxins and furans and Lindane and 2,4-Dichlorophenyxoacetic Acid (2,4-D).

Pre-treatment: Contaminants must be in gaseous form for a GPCR reactor to reduce them. While liquid wastes can be preheated and injected directly into the reactor on a continuous basis, contaminants on solids must first be volatilized from the solids. Bulk solids and drummed chemicals are placed in a TRBP, which is then heated to approximately 650°C in a hydrogen-rich (oxygen deficient) atmosphere. In this environment, the contaminants are desorbed (leaving a hazard-free solid) and are then conveyed directly to the GPCR reactor for destruction.

Because the TRBP involves minimal handling (i.e., material need not be removed from drums and does not require sorting or segregation by type), worker exposure to the chemicals is minimal.

An evaluation for the US Department of Energy (DOE) noted that the front-end components for introducing solids and large equipment was a limiting factor. A more recent assessment of the applicability of GPCR for chemical weapons destruction noted that the TRBP should be "completely effective in decontaminating metal components" to the stringent requirements of the ACWA program and that "[a]n advantage of the GPCR process with regard to solids treatment is that the solids would not have to be size-reduced or shredded before being treated. Treatment could be as simple as removing the lids from the solids waste drums and treating the drums in the TRBP."

Depending on the waste type, one of the following three pre-treatment units is currently used to volatilize wastes prior to treatment in a GPCR reactor:

(a) Thermal reduction batch processors (TRBPs) for bulk solids, including those in drums;
(b) Toroidal bed reactors for contaminated soils and sediments, but also adapted for liquids;
(c) Liquid waste pre-heater systems (LWPSs) 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 metre.

Emissions and residues: In addition to hydrogen chloride and methane, low molecular weight hydrocarbons may be emitted. This gas leaving the GPCR reactor is scrubbed in two caustic scrubber towers to cool the gas and to remove acid, water, heat and fine particulate. The acid in the gas (HCl, in the case of chlorinated wastes) can be neutralized with a caustic solution (to create a salty scrubber water), or recovered for subsequent refinement/concentration to recyclable specifications for industrial reuse.

The cooled and scrubbed product gas is a mixture of hydrogen, methane, carbon monoxide and other light hydrocarbons. Some of the product gas is reheated and recirculated back to the reactor, or through the TRBP as sweep gas. Excess product gas is removed from the system, compressed and temporarily stored. This stored product gas is chemically tested with on-line instruments and then used as fuel to heat system components such as the boiler, and as an input stream to a catalytic steam reformer as heating fuel for hydrogen generation (in situations where piped hydrogen gas is not readily available at the site). This gas meets the BIF standards for use as a fuel in the United States.

Residues from the GPCR process include used liquor and water. Solid residues will also be generated from solid waste inputs. Since the GPCR process takes place in a reducing atmosphere, the possibility of PCDD and PCDF formation is considered limited. The system does not produce slag or ash – the only solid process residual (other than the treated steel and other treated waste inputs) is carbon filter media, which are not a system output. When the filters are "spent", they are placed in the TRBP, which heats them to desorb contaminants, and the contaminated gas goes to the GPCR reactor for destruction. The carbon is now ready for reuse, as is common practice at GPCR commercial operations.

During disposal of approximately 500 tonnes of pesticides and 1500 tonnes of PCBs in Kwinana, no PCBs or DDT was detected in gaseous, liquid and solid outputs. Further, during regulatory testing waste-specific compounds were not detected in air, solid and liquid outputs and no slag was created.

Release control and post-treatment: 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.

Energy requirements: Methane produced during the GPCR process can provide much of the fuel needed in the process. It has been reported that electricity requirements range from 96 kWh per tonnes of soil treated to around 900 kWh per tonnes of pure organic contaminants treated.

Material requirements: 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.

Portability: GPCR is available in fixed and transportable configurations.

Health and safety: Use of hydrogen gas under pressure requires suitable controls and safeguards to ensure that explosive air-hydrogen mixtures are not formed. Operating experience gained to date has indicated that the GPCR process can be undertaken safely. GPCR is used to treat sewage sludge by converting the waste into clean water and a clean hydrogen enriched methane gas while chemically destroying all pathogens and pharmaceuticals and recovering phosphorous. There are no fugitive methane emissions in the process.

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

(a) TRBPs have a capacity of up to 100 tonnes of solids per month or up to four liters per minute of liquids. Two TRBPs can be used in parallel to double capacity;
(b) Toroidal bed reactors have a capacity of up to 5,000 tonnes of soils and sediments per month, although these pre-treatment units are still in the development stage; and
(c) LWPSs have a capacity of three liters per minute.

Throughput of the technology will depend on the scale of the GPCR plant that is deployed, and the type of waste being treated. The following table gives the rough throughput estimates for different waste types. A general description of the different plant sizes follows the table.

Waste Type	**Plant**	**Capacity (t/year)**
PCB Oil	Semi-Mobile	840
	Full Scale	3,360
CFCs and Halons	Semi-Mobile	1,680
	Full Scale	6,720
PCB Capacitors	Semi-Mobile	1,400
	Full Scale	5,600

Chlorinated Pesticides (solid and/or liquid)	Semi-Mobile	840
	Full Scale	3,360

POPs throughput: [POPs waste/total waste in %]: Most GPCR experience has been with the treatment of chlorinated POPs wastes (PCBs, pesticides) and to a lesser degree fluorinated wastes (chemical warfare agents and chlorofluorocarbon refrigerants). The technology has also been used to treat a small quantity of iodic waste. In general the technology is well suited and well proven for halogenated waste streams.

Of particular benefit is the fact that the waste streams do not require dilution prior to destruction using GPCR. For example, in April 1999 the technology was used to treat almost 84% pure hexachlorobenzene crystals using the commercial-scale GPCR plant in Kwinana; no dilution or specialized pre-treatment was required. Similarly, the refrigerant R-12 (dichlorodifluoromethane) was treated in pure form (100% strength) using the GPCR demonstration plant. This robustness is an advantage over other technologies that may require dilution of the material to accommodate the high halogen content.

Summary of high-strength POPs treated**:**

- Commercial testing at Kwinana, Australia: 30.3% DDT, 5.6% DDT, 96% PCBs (1995/1996)
- Commercial testing at General motors with 50% PCBs and 30% Chlorobenzenes (1996)
- Commercial demonstration at Kwinana, Australia: 84% Hexachlorobenzene crystals (April 1999)
- Demonstration with portable plant at Rockwood, Canada: 100% dichlorofluoromethane gas (2002)
- Demonstration with portable plant at Rockwood, Canada: 100% Lindane powder (2003)

Costs:

Site preparation costs [US Dollars]: Estimated Capital Costs (unburdened design labour, no licensing/royalties, includes installation and commissioning, site preparation):

- Two-TRBP Plant Estimate (solid feed):
  Full-Scale $10,800,000
  Semi-Mobile $ 5,000,000
- One-TRBP Plant Estimate (liquid and gaseous feed):
  Full-Scale $10,300,000

Semi-Mobile $ 4,750,000

- Estimate of Utility and Labour Costs for Pesticide Treatment (estimates based on 2004 US utility prices)

Waste Type	Plant	Capacity waste feed (US$)*	Estimated GPCR cost per tonne of (t/year)	
			Utilities	Labour
Chlorinated Pesticides (solid or	Semi-Mobile	840	$1,317	$593

liquid)	Full Scale	3,360	$1,317	$222

* Utility and Labour costs are marginal only; no allocation has been made for overhead or profit

- Decommissioning costs: Estimated at $750,000
- Landfill costs: Depending on the local situation – Should be filled in by the concerned country

Other practical issues: Contaminants such as sulfur and arsenic were found to inhibit treatment in earlier development stages, although it is unclear whether this problem persists.

State of commercialization: Commercial-scale GPCR facilities have operated in Canada and Australia. The GPCR facility in Australia operated for more than five years until 2000. In the United States, there is a plan to build a GPCR synthetic diesel facility in Fauquier County, Virginia, with a daily processing capacity of 200 Mg.

Summary:

- Demonstrated in pilot and small commercial facilities in developed countries.
- Fixed and mobile configurations available.
- Require secure infrastructure, trained technical staff, laboratory support, utilities and reagent supply.
- High level of complexity including safe handling of hydrogen.

3. Plasma Arc[18]

Process description: The waste, as a liquid or gas, is injected directly into the plasma and is rapidly (<1 ms) heated up to about 3,100°C and pyrolysed for about 20 ms in the water-cooled reaction chamber (flight tube). The high temperature causes compounds to fully dissociate into their elemental ions and atoms. Recombination occurs in a cooler area of the reaction chamber, followed by a quench, resulting in the formation of simple molecules. The plasma arc system requires a mono-nitrogen oxides (NOx) abatement device, as important amounts of NOx are produced by the high temperature flame.

The guidance on BAT/BEP developed by the Stockholm Convention relevant to Article 5 and Annex C should be used and applied to this technology (UNEP).

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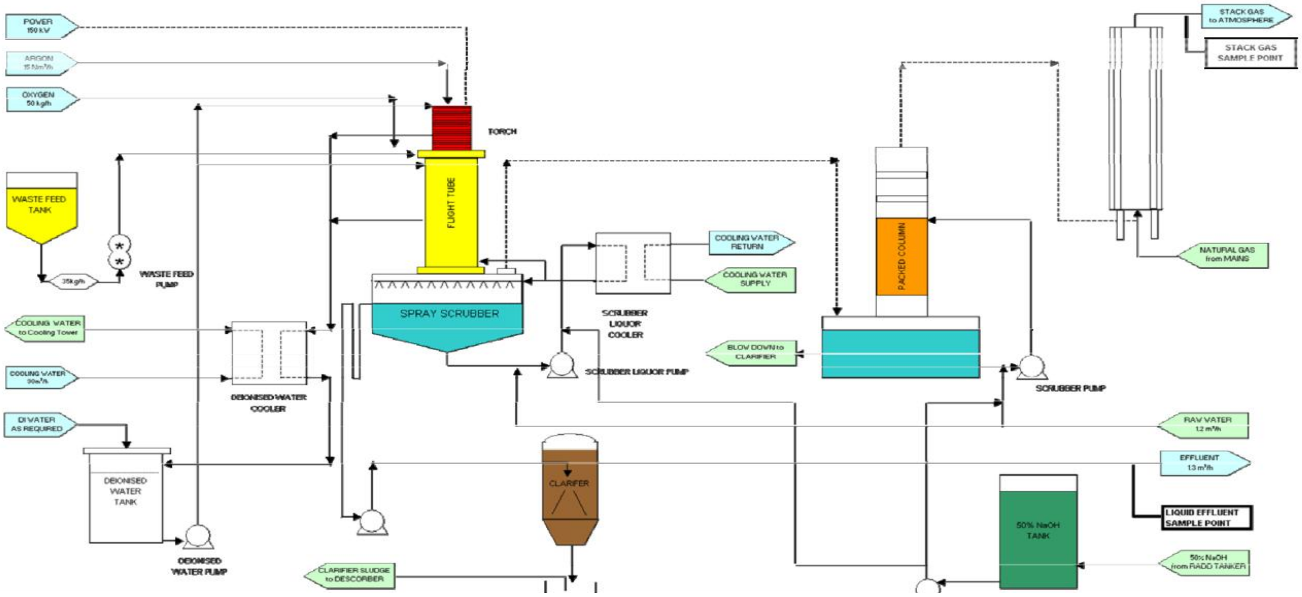
[18] See UNEP, 2017, UNEP, 2002

Process Diagram (Ex. PLASCON):



Efficiency: Bench-scale tests with oils containing 60 % PCBs have achieved DREs ranging from 99.9999-99.999999 %. A DE of 99.9999 % is achievable for most pesticide POPs, including chlordane, chlordecone, DDT, endosulfan and heptachlor. Independent performance monitoring data has shown that DEs for POPs and ODSs are consistently greater than 99.9999%. The concentration of residual POPs in the treated effluent stream is typically not detectable, at a detection level of 0.5 µg/L and atmospheric emissions are typically less than 1µg/Nm3. Dioxin emissions are typically less than 0.01 ng-TEQ/Nm3. Japanese control levels to the treated effluent streams (gas and liquid) are very rigorous. Facilities have adsorption vessels of activated carbon treatment for both gas and liquid effluent streams. PCBs removal rate from the concentrate solution to the effluent streams is typically greater than 99.999999 %.

Waste types: Plasma arc system facilities have been used to treat a wide range of PCBs, pesticide POPs, halons and chlorofluorohydrocarbons. Waste types to be treated must be liquid or gas, solids must first be pre-treated to fine slurry that can be pumped. Very viscous liquids or sludges thicker than 30–40 weight motor oil cannot be processed without pre-treatment. Other solid wastes cannot be treated unless some form of pre-treatment is undertaken.

Pre-treatment: Pre-treatment is not required for most liquids. Solids such as contaminated soils, capacitors and transformers can be pre-treated using thermal desorption or solvent extraction. Liquid streams should not contain particles greater than 0.5 mm in size. A Thermal Desorber is used to remove contaminants from solids. The contaminants are condensed and treated in liquid or gaseous phase. Typical solids treated are: transformer and capacitor parts, protective clothing, contaminated drums and packaging and soil. Liquid POPs can be directly injected. POPs formulated with solids are desorbed first and then fed as liquid or vapour.

Emissions and residues: Emissions include gases consisting of argon, carbon dioxide and water vapors. Residues include an aqueous solution of inorganic sodium salts, such as sodium chloride, sodium bicarbonate and sodium fluoride. Traces of PCDD and PCDF have been detected in effluent gas from plasma arc systems. These traces are at a concentration of less than 0.01 ng TEQ/Nm^3. POP concentrations in solid residues are unknown.

Release control and post-treatment: Currently, there is little information available regarding post-treatment requirements.

Energy requirements: A 150 kW plasma arc system unit requires 1,000–3,000 kWh of electricity per tonne of waste treated.

Material requirements: Currently, there is little information available regarding material requirements. It has been noted, however, that this process requires argon gas, oxygen gas, caustic and cooling water.

Portability: Plasma arc systems are available in both portable and fixed units.

Health and safety: Since the plasma arc system process has a low throughput, there is a low risk associated with the release of partially treated wastes following process failures. Currently, there is little additional information available regarding health and safety.

Capacity: A 150 kW plasma arc system unit can process 1–3 tonnes of POPs waste per day.

Costs: Standard 150KW (Ex. PLASCON Plant) approx. $USD 1.5 million. Operating & Maintenance Costs $USD 2,000 per tonne for Schedule Wastes.

Other practical issues: It should be noted that metals or metal-like compounds (e.g. arsenic) may interfere with catalysts or cause problems in disposing of residues. For example, arsenicals in pesticide waste exported from Pacific islands for disposal in Australia using the plasma arc system process have presented problems.

State of commercialization: BCD Technologies Pty Ltd. operates two plasma facilities in Australia: one in Brisbane for PCBs and other POPs and another one in Melbourne for treating CFCs and halons. BCD Technologies Pty Ltd. also operates a BCD facility for low-level PCBs and POPs and has two thermal desorbers for treating contaminated solids.

Summary:

- Commercially available technology with a number of operating facilities in developed countries.
- Technology vendors with stable licensee arrangements capable of competitive tendering worldwide.
- Fixed and mobile facilities potentially available.
- Require secure infrastructure, trained technical staff, laboratory support and utilities and re-agent supply.
- High level of complexity

4. Pyrolysis/ Gasification[19]

These technologies attempt to separate the components of the reactions that occur in conventional waste incineration plants by controlling process temperatures and pressures in specially designed reactors.

Typical reaction conditions and products of combustion, pyrolysis and gasification processes

	Combustion	**Pyrolysis**	**Gasification**
Reaction temperature (ºC)	800–1,450	250–700	500–1,600
Pressure (bar)	1	1	1–45
Atmosphere	Air	Inert nitrogen	Gasification agent: O_2, H_2O
Stoichiometric ratio	> 1	0	< 1
Products from the process			
• Gas phase:	CO_2, H_2O, O_2, N_2	H_2, CO, hydrocarbons, H_2O, N_2	H_2, CO, CO_2, CH_4, H_2O, N_2
• Solid phase:	Ash, slag	Ash, coke	Slag, ash
• Liquid phase:		Pyrolysis oil and water	

As well as specifically developed pyrolysis/gasification technologies, conventional incineration technologies (i.e. grates, fluidised beds, rotary kilns, etc.) may be adapted to be operated under pyrolytic or gasifying conditions, i.e. with reduced oxygen levels (sub-stoichiometric), or at lower temperatures. Often pyrolysis and gasification systems are coupled with downstream combustion of the synthesis gas generated.

Besides the general objectives of waste incineration (i.e. effective treatment of the waste), the additional aims of gasification and pyrolysis processes are to:

- convert certain fractions of the waste into process gas (called synthesis gas or syngas);
- reduce gas cleaning requirements by reducing flue-gas volumes.

Both pyrolysis and gasification differ from combustion in that they may be used for recovering the chemical value of the waste (rather than its energetic value). The chemical products derived may in some cases then be used as feedstock for other processes. However, when applied to wastes, it is more common to combine the pyrolysis, gasification and combustion process, often on the same site as part of an integrated process. When this is the case, the installation recovers the energy value rather than the chemical value of the waste, as a conventional incinerator would.

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[19] See *European Commission, 2018*

In some cases, the solid residues arising from such processes contain pollutants that, in an incineration system, would be transferred to the gas phase, and then, with efficient flue-gas cleaning, be removed with the FGC (Flue Gas Clean-up) residue.

Pyrolysis is the degassing of wastes in the absence of oxygen, during which pyrolysis gas and a solid coke are formed. The heat values of pyrolysis gas typically lie between 5 MJ/m^3 and 15 MJ/m^3 based on municipal waste and between 15 MJ/m^3 and 30 MJ/m^3 based on RDF (Refuse-derived fuel). In a broader sense, 'pyrolysis' is a generic term including a number of different technology combinations that constitute, in general, the following technological steps:

- *Smouldering process*: Formation of gas from volatile waste particles at temperatures between 400°C and 600°C.
- *Pyrolysis*: Thermal decomposition of the organic molecules of the waste between 500°C and 800° C, resulting in the formation of gas and a solid fraction.
- *Gasification*: Conversion of the carbon share remaining in the pyrolysis coke at 800°C to 1,000 °C with the help of a gasification substance (e.g. air or steam) in a process gas (CO, H_2).
- *Incineration*: Depending on the technology combination, the gas and pyrolysis coke are combusted in an incineration chamber.

Process description: Two different types of *pyrolysis-gasification processes* can be distinguished:

- disconnected (pyrolysis with subsequent gasification = conversion process); and
- directly connected.

Conversion process
In the conversion process, metals and, if required, inert material may be removed after the pyrolysis step. As pyrolysis gas and pyrolysis coke require reheating in the gasification process, the technical and energetic requirements are higher than with connected processes. The condensed exhaust vapour is treated as waste water and discharged.
In the conversion process, the waste needs to be shredded and dried before it can be used in the first thermal stage. This stage more or less corresponds to that of the 'smoulder-burn' process. The subsequent stages are:

- pyrolysis in the kiln;
- removal of solid residues;
- separation of the fine fraction enriched with carbon;
- sortingof the metal and inert fraction.

The pyrolysis gas is cooled to condense exhaust vapors and pyrolysis oil. It is then supplied, together with the pyrolysis oil and the fine fraction, to the second thermal stage, which is a current flow gasifying reactor. The oil and the fine fraction are gasified in the current flow at high pressure and at a temperature of 1,300° C. The resulting syngas is cleaned and then combusted for energy recovery. Solid residues are withdrawn as melted granulate through a water bath. They correspond in type and quantity to those from the 'smoulder-burn' process.

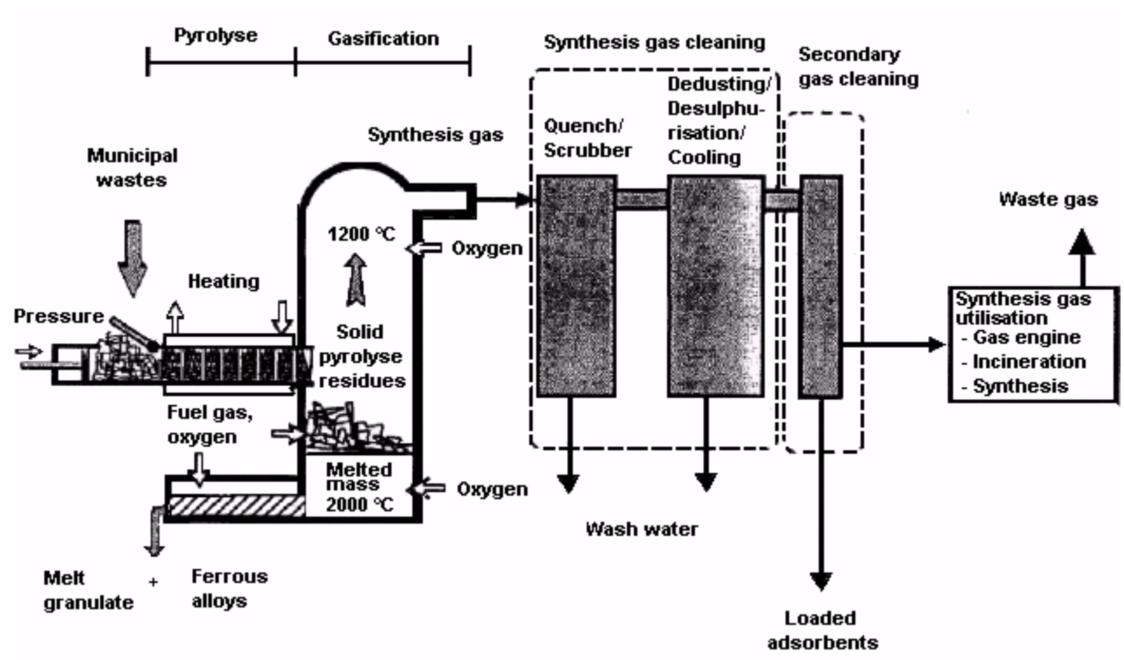
Direct connection process
With direct connection, there may be improved electricity generation rates, but the metals and inert material go into a melt for which no use has been found to date.

Combined gasification-pyrolysis and melting process
In such processes, the unshredded wastes are dried in a push furnace and partially pyrolysed. From this furnace they are transferred directly and without interruption into a standing packed bed gasifier. Here they are gasified (in the lower part) at temperatures of up to 2,000°C with the addition of oxygen. Pure oxygen is also added in the upper part of the gasification reactor to destroy the remaining organic components in the generated syngas, through oxidation, gasification and cracking reactions.

Although reported to be capable of treating a wider range of wastes, this process is mainly used for municipal and non-hazardous industrial wastes. Wastes with a LHV (Lower heating value) of 6–18 MJ/kg and moisture content up to 60% may be treated. Automotive shredder residues with a chlorine content of up to 3.5 % have been treated with approximately equal amounts of MSW (Municipal solid waste).

The syngas is subjected to a gas cleaning process and then combusted to utilize the energy value. The originally solid residues leave the reactor molten. During test operations, approximately 220 kg of bottom ash with approximately 30 kg metal accumulated per tonne of waste input was generated.

Schematic diagram of a push pyrolyser (example shown operated by Thermoselect)



Two plants of this type were operated in Japan as of 2003. Two plants of this type were also built in Europe but ceased operation after some years.

Summary:

- Commercial units from a number of technology vendors but limited application to POPs wastes.
- Subject to demonstration of stable licensee arrangements should be capable of competitive tendering worldwide.
- Fixed and mobile facilities potentially available.

- Require secure infrastructure, trained technical staff, laboratory support and utilities and reagent supply.
- High level of complexity.
- Moderate power consumption with reliable water and electrical supply
-

5. GeoMelt™[20]

Process description: This process is applicable not for common waste disposal but mainly for the in-situ treatment of contaminated sites. The GeoMelt™ process works by establishing a melt between pairs of electrodes inserted into the soil-bound waste materials. Initially, electrical current is passed through a relatively high-conductivity starter path staged in the soil/waste matrix. Heat dissipated in the starter path is transferred to the surrounding soils causing them to melt. Once molten, the soil becomes sufficiently conductive to support the flow of electrical current, thereby dissipating enough joule heat to sustain and propagate the melting process. Electrical energy is continuously supplied to the melt until such time that it has grown to encompass the entire treatment volume. Individual melts of up to approximately 1,000-tonnes can be formed. These range in size from 9 to 11 meters in diameter and up to 5 meters thick. With the GeoMelt™ Subsurface-Planar Vitrification method, the melting process can be initiated at virtually any depth below grade, and can be propagated from this initial start-up depth to the desired treatment depth.

Off gases generated by the process are collected inside a stainless-steel hood covering the treatment area and are drawn off for processing by an off-gas treatment system (OGTS). The OGTS consists of a combination of filtration, dry & wet scrubbing, and thermal treatment stages. The small quantity of secondary wastes generated by the OGTS (e.g.–filters, scrubber liquids, and personal protective equipment) can be loaded into subsequent GeoMelt™ applications for processing.

When electrical power is shut off, the molten mass cools and ultimately solidifies into a vitreous and crystalline, rock-like monolith. The process destroys organic contaminants such as dioxins, pesticides, and PCBs directly. Heavy metals, radionuclide, and other non-volatile constituents are retained in the melt and immobilized in the vitrified monolith. The vitrified product has exceptional physical, chemical, and weathering properties compared to alternative solidification/stabilisation technologies. It is typically ten times stronger than concrete and is extremely leach resistant.

The GeoMelt™ process generates a vitrified product that is far superior (orders of magnitude better) in terms of durability, strength, and leach resistance compared to other stabilisation or encapsulation technologies. The monolith can be safely left in place. Alternatively, it can be readily recovered for transport to a disposal site. In certain applications, the vitrified product can be recycled for subsequent use (e.g. – roadbed materials, breakwater riprap, and roofing tiles).

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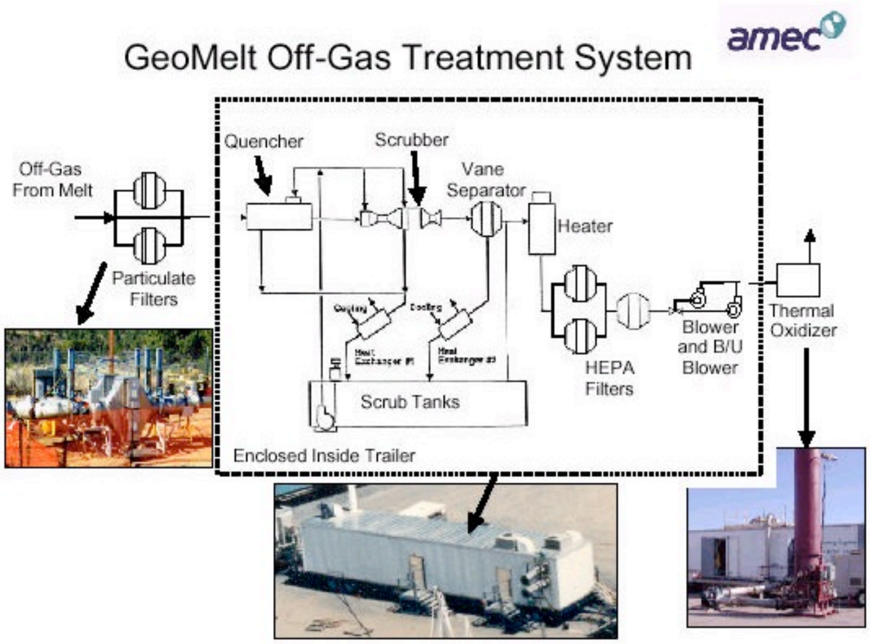
[20] Vijgen J., 2002, NATO/CCMS Pilot Study Evaluation of Demonstrated and Emerging Remedial Action Technologies for the Treatment of Contaminated Land and Groundwater (Phase III), GeoMelt™ Vitrification process

Process diagram:



Note to process diagram: The oxidiser is shown at the end of the system in this instance. In most cases the oxidiser is put immediately after the high temperature filters and then a quench.

Performance: Treatment efficiency: To date, over 25,000 tonnes of contaminated soil and debris have been successfully remediated using the GeoMelt™ process. Examples of typical chemically-contaminated sites remediated with the GeoMelt™ process include:

- 4,350 tonnes of soil and debris contaminated with pesticides (e.g. chlordane, DDT, dieldrin, and small concentrations of dioxins and furans) and heavy metals (e.g. arsenic, cadmium, chromium, lead, and and mercury) in Grand Ledge, Michigan USA;
- 7,000 tonnes of PCBs-contaminated soil and debris at a transformer repair site in Spokane, Washington USA;
- 5,440 tonnes of soil and debris contaminated with dioxins, pentachlorophenol, DDT, 2,4-D, hexachlorobenzene, and a range of other pesticides and herbicides at a chemical waste site near Salt Lake City, Utah USA.

Two further examples include sites contaminated with radioactive materials that were successfully remediated using the GeoMelt™ process of 5,400 tonnes of soil, steel, barytes bricks, and other debris contaminated with plutonium and uranium at the Maralinga Taranaki Pits in southern Australia and 500-tonnes of soil and cobble contaminated with plutonium, uranium, americium, heavy metals, and phosphates.

In addition to these in-situ applications, a series of GeoMelt™ In-Container Vitrification (ICV) demonstrations were performed in Australia on soils contaminated with 33wt% hexachlorobenzene (HCB) wastes. The successful results obtained from these tests have led to the design and construction of a facility to process the 16,000 208-L drums of HCB wastes present at a chemical processing plant there.

The GeoMelt™ process achieves very high destruction/retention efficiency (DRE) in the melt, which is the first step of the overall treatment process. The high temperature of the melt promotes pyrolysis and dechlorination reactions in the hot soil surrounding the melt. Consequently, organic destruction efficiencies ranging from 90 to 99,99% have been demonstrated by the melt itself in the GeoMelt™ process. Heavy metals, radionuclides, and other non-volatile constituents present in the soil/waste matrix are retained in the vitrified product where they are immobilised and effectively isolated from the surrounding ecosystems for perpetuity.

Off-gases generated during GeoMelt™ processing are collected within the stainless steel off-gas hood placed over the treatment zone. These are piped to the OGTS for subsequent processing. The wet and dry treatment systems making-up the OGTS contribute to further destruction and/or removal of the trace quantities of contaminants present in the off-gas flow. When combined with the destruction efficiency of the melt itself, overall DREs in the range of 99.99 to 99.9999% have been demonstrated by the GeoMelt™ process for a wide range of hazardous organic and inorganic contaminants. Consequently, the concentration of hazardous chemical constituents present in the off gas at the stack exit is typically at or near detection limits, and is two or more orders of magnitude below acceptable emission limits.

For example, at the Parsons Chemical Site in Grand Ledge, Michigan USA, initial soil concentrations of 4,4'-DDT (340,000 ppb) and dieldrin (4,600 ppb) were reduced to non-detect levels in the vitrified product. This is to be expected as neither of these compounds can survive the extreme thermal conditions imposed by the GeoMelt™ vitrification process. Analysis of the concentration of these constituents in the stack emissions generated during processing indicated non-detect levels. Prior to GeoMelt™ processing, samples of the site soils were subjected to Toxicity Leach Test Procedure (TCLP) testing to assess its propensity for leaching heavy metals. The vitrified product generated by the GeoMelt™ process was also subjected to TCLP testing for this purpose. The concentration of arsenic, barium, chromium, and lead present in the leachate from these tests was 8 to 1300 times lower for the vitrified product than for the site soil. In all cases, the concentration of these heavy metal constituents present in the leachate generated by applying the TCLP procedure to the vitrified product was well below the established regulatory limits.

At the TSCA Demonstration Test Site in Spokane, Washington USA, the concentration of PCBs in the contaminated soil at the Site ranged from 170 ppm to over 17,860 ppm, with the average concentration being 14,377 ppm. The PCB concentration found in the vitrified product was below detection limits. Moreover, soil samples obtained from areas surrounding the vitrified block indicated no detectable concentration of PCBs, dispelling the notion that these contaminants can migrate away from the advancing melt front into the surrounding, non-contaminated soils. Samples obtained from the off-gas stack exit during processing were analysed to determine the presence of PCBs and TCDD equivalents. In all cases, the concentrations were essentially non-detect, with concentrations not statistically different from background, ambient airborne concentrations. The off-gases were also analysed to determine the concentration of polynuclear aromatic hydrocarbons (PAHs – e.g., naphthalene, fluorene, phenanthrene, fluoranthane, and pyrene) and other VOCs (Volatile organic compounds). The measured concentrations were in the low ppb range for these constituents. Consequently, the concentrations were typically three orders of magnitude below their respective accepted NIOSH exposure limits. Finally, the off-gas effluent was analysed for particulates, chloride, CO, and

NOx emissions. PM10 particulate emissions were in the range of 0.23 to 7 mg/dscm (milligrams per dry standard cubic meter); HCl emissions were in the range of 0.6 to 14 ppm. These emission levels are at least one order of magnitude lower than US federal guideline values. NOx emissions were in the range of 30 to 40 ppm; CO concentrations were below detection limits. Again, these values are well below established guideline levels. These combined results indicated that the overall PCB DRE for the process ranged from greater than 99.99962% to greater than 99.99998%. Discounting the off-gas treatment system's contribution to the overall DRE, these results indicate the PCB DRE for the melt itself was in the range of 97.11 to 99.77%.

Tests in Australia involving applying the GeoMelt™ In-Container Vitrification process to treatment of soil contaminated with 33 wt% HCB yielded an overall DRE of 99.9999%. When the influence of the off-gas treatment system is removed from this value, a DRE of 99.75% is obtained for the melt itself. The off-gas effluent at the stack was sampled and analysed during this test. The results indicated concentrations of 89 ppb for HCB, 1.2 ppm for bis(2-ethylhexyl) phthalate, and non-detect (less than 72 ppb) levels for the dichlorobenzene isomers, 1,2,4-trichlorobenzene, hexachloroethane, napthalene, and hexachlorobutadiene. Total VOCs and HCl concentrations in the off-gas effluent were less than 1.5 ppm and 0.7 ppm, respectively. Particulates were measured at 3.3 mg/dscm in the off-gas effluent. The concentration of CO in the off-gas effluent was in the range of 2 to 4 ppm, while NOx concentrations ranged from 27 to 74 ppm.

Throughput: The existing US and Australian GeoMelt™ large-scale vitrification systems have a demonstrated process rate of approximately 90 tonnes per day when applied to in-situ applications. Depending upon the composition and configuration of the waste matrix, a typical 800 tonnes large scale in situ melt requires approximately 10 to 14 days of operation. The US GeoMelt™ InContainer Vitrification unit can process wastes at a nominal rate of 45 tonnes per day. The Japanese GeoMelt™ staged-batch facility has a demonstrated process rate of approximately 30 tonnes per day. When completed, the Australian GeoMelt™ InContainer Vitrification facility will process at a nominal rate of 25 tonnes per day.

Wastes/Residuals: Typical waste streams generated by the GeoMelt™ process include scrub solution, particulate and carbon filter media, and personal protective equipment (e.g. gloves, coveralls, and respirator cartridges). The quantities generated in each application are very case-specific. Solid secondary waste materials are typically staged in subsequent melts. Scrub solution can be condensed by evaporating excess water during the final stages of operation. Consequently, typical waste volumes for this component are on the order of 5,000-10,000 liters. These volumes are per project, not per melt.

Reliability: To date, all commercial GeoMelt™ applications have successfully and completely processed the entire target volume of hazardous chemical wastes to which it has been applied.

Limitations: As the commercial experience described above indicates, the GeoMelt™ process is very robust. It can be applied to a broad spectrum of contaminants in a wide range of configurations. There are conditions in which some pre-treatment activities are appropriate, however. For example, in situations wherein there exists excessive moisture levels in the waste form (i.e. super-saturated), the GeoMelt™ process is most effectively employed if this moisture is first reduced to at most fully-saturated levels by some other means (e.g. pumping, drying, and/or sorbing the excess moisture onto additional soil). When the potential exists for significant groundwater recharge during processing, precautionary measures should be invoked prior to

GeoMelt™ processing to either prevent or redirect the groundwater flow. This can be done by conventional methods in common use in the industry. For example, a system of wells placed can be installed at strategic locations around the region targeted for GeoMelt™ processing to alter the site's hydrological conditions. Alternatively, diversion barriers can be inserted up-gradient from the region targeted for GeoMelt™ processing so that the groundwater flow is suitably redirected.

The GeoMelt™ process should also not be applied to direct processing of waste streams containing sealed containers of volatile materials. In these situations, the sealed containers should be punctured or otherwise compromised to preclude a build-up of pressure within the container during processing. In both instances, the required pre-treatment technologies are readily available in the industry and represent only marginal additions to the overall treatment cost.

Transportability: The US and Australian GeoMelt™ vitrification and off-gas treatment systems are transportable over the roadways via common carrier. The Japanese GeoMelt™ and Australian GeoMelt™ HCB-Processing plants are fixed-base facilities, however. They are located near Ube City, Japan and Adelaide, Australia, respectively.

Detailed information: The references listed at the end of this document provide extensive operational and analytical data for each of the commercial applications to which the GeoMelt™ process has been applied.

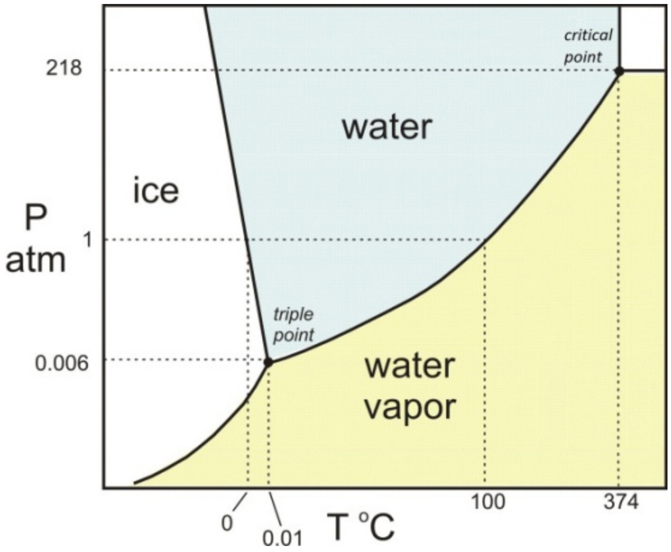
Summary: The GeoMelt™ vitrification process has been successfully applied to remediate numerous hazardous waste sites and materials in the US, Australia, and Japan. The process has been in commercial application since the early 1990s. It can be applied to a wide range of organic and inorganic contaminants, including virtually all pesticides, herbicides, PCBs, solvents, and heavy metals. The GeoMelt™ process has also been applied to remediation of radioactively contaminated wastes.

The process is very robust. It can treat a broad spectrum of waste materials, simultaneously, without the need for separation and/or segregation prior to processing. In some situations, limited pre-treatment of the waste zone and surrounding area may be required to reduce excess moisture in the waste stream below super-saturated levels. This may also be required in some applications to insure that direct processing volatile materials trapped inside sealed containers or between impermeable barriers and the advancing melt is precluded.

- Commercial operating facilities in a number of developed countries.
- Require secure infrastructure, trained technical staff, laboratory support and utilities and re-agent supply.
- Technology vendor with stable licensee arrangements capable of competitive tendering worldwide.
- High power consumption.
- High level of complexity.

6. Supercritical water oxidation (SCWO) and subcritical water oxidation

Supercritical water is water that is heated and pressurized above its thermodynamic critical point of 374°C and 218 atmospheres. The system operates at 650°C to ensure complete oxidation of wastes.



Process description[21]: SCWO and subcritical water oxidation treat wastes in an enclosed system using an oxidant (such as oxygen, hydrogen peroxide, nitrite, nitrate, etc.) in water at temperatures and pressures above the critical point of water (374°C and 218 atmospheres) and below subcritical conditions (370°C and 262 atmospheres). Under these conditions, organic materials become highly soluble in water and are oxidized to produce carbon dioxide, water and inorganic acids or salts. For improved organic waste destruction the system can operate at a temperature of 650°C and a pressure of 23.5 Mpa. The high reaction kinetics ensures high destruction efficiency (non-detect) of the organic waste.

For example, General Atomics Electromagnetic Systems Industrial Supercritical Water Oxidation (GA-EMS iSCWO) system[22] uses compressed air rather than more expensive pure oxygen (O2) in the treatment process to reduce safety concerns and practices. The iSCWO process makes most organic materials, oxidation reactants, and oxidation products miscible in water, allowing complete oxidation reactions to take place at a high rate. The result is the creation of CO_2, water and salts, all of which can be released into the environment or reused for other industrial purposes without any post treatment. NOx1, SOx, and particulate concentrations created are also at or below detection limits.

GA's iSCWO system is suited for onsite organic waste destruction, does not require any afterburner or complex secondary off-gas processing system, is a simple system that is easily maintainable, and designed for little or no liquid post-treatment prior to discharge to a publicly

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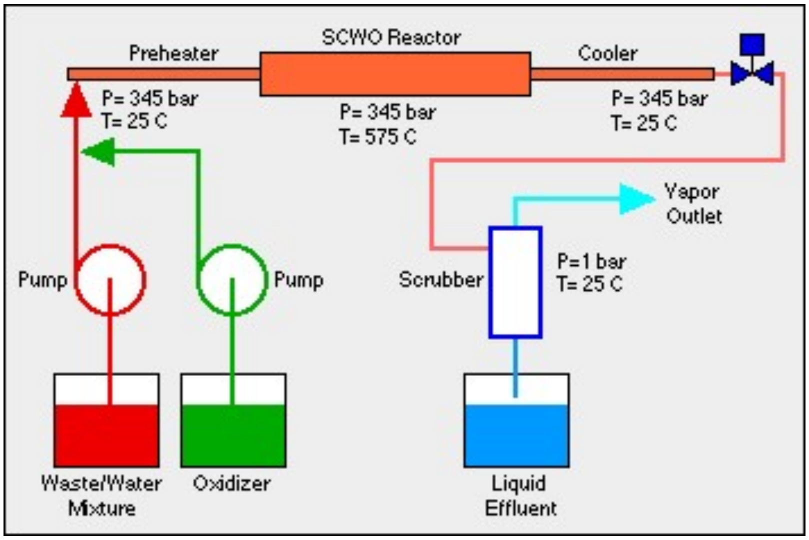
[21] See *UNEP, 2017*

[22] General Atomics, Industrial Supercritical Water Oxidation (iSCWO)

owned treatment works. Heteroatoms such as chlorine, fluorine, phosphorus and sulfur are converted to inorganic acids or to salts if sufficient cations such as sodium or potassium are present. If present, metals such as iron and copper will produce metal oxides. Typical iSCWO gaseous discharge composition when oxidizing organic compounds consists of depleted oxygen, carbon dioxide and water vapor.

Typical SCWO Process Flow Diagram



Treatment Advantages

- Efficient waste destruction at 23.5 Mpa and 650˚C to 700˚C
- Can treat concentrated to very dilute liquid wastes
- Very rapid, thorough destruction of organics; therefore, *no Pollution Abatement System (PAS) required in most cases*
- Effluents containing very low nitrogen oxide (NO_X), sulfur oxide (SO_X), and total organic carbon (TOC) content
- Low excess air requirement
- Destruction efficiency of TOC >99.99% (non-detect)

Efficiency[23]: DEs greater than 99.999 % and DREs greater than 99.9999% have been reported for chlordane, DDT and PCBs for SCWO. According to Downey K. (2007) was conducted a testing at a reactor temperature and pressure of ~650°C and 218 atmosphere, respectively. Liquid and gas samples were collected during the test per approved EPA methodology and then analyzed to determine the PCB, dioxin, and furan content. In the liquid samples, no PCBs, dioxins, or furans were detected. In the gas samples, 17 separate dioxins/furans were evaluated. Fourteen of the 17 were below detection limits. The remaining three were detected at extremely low concentrations. SCWO has been shown to be effective in the treatment of toxic chlorinated chemicals such as

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[23] See *UNEP, 2017*

PCBs, pesticides and flame retardants[24]. Overall, SCWO usually has a DE greater than 99.99 % for a wide range of organics (General Atomics).

Waste types[25]: SCWO and subcritical water oxidation are thought to be applicable to all POPs. Applicable waste types include aqueous wastes, oils, solvents and solids with a diameter of fewer than 200 µm. For improved organic waste destruction the system can operate at a temperature of 650°C and a pressure of 23.5 Mpa. The high reaction kinetics ensures high destruction efficiency (non-detect) of the organic waste.

SCWO is excellent for the destruction of:

- Expired or obsolete pesticides, fertilizers, and fungicides
- Contaminated water (waste water cleanup)
- Expired or obsolete paints
- Petroleum and/or petrochemical waste streams
- Polychlorinated biphenyls (PCBs)
- Organic cleaning solutions
- Sewage sludge/animal waste products

Energetic material (explosives or propellant)*Pre-treatment*: Concentrated wastes may have to be diluted prior to SCWO treatment in order to reduce their organic content to below 20% by weight. This increases considerably the waste volume to be treated. Other processing options include addition of fuel to low concentration, low calorific value wastes, co-processing of dilute and concentrated wastes and partial sludge dewatering, among others. Solid material will be ground up through a grinder followed by a micronizer to be slurry pumped into the SCWO. The entire process and pumping would be using water as the working fluid to transport the slurry material to the iSCWO system[26]. Generally the maximum percentage by weight is around 25% - but this can be verified for testing. The particle size is about 0.5 mm – this size is to make sure there is complete organic destruction and as the feed pipe into the reactor is on the order of 1 mm.

Emissions and residues: Under operating conditions above the critical range of 500°C - 650°C and 25 MPa with reactor residence times under one minute for complete destruction PCDD/PCDF, NOx and other toxic by-products are not formed in SCWO. However, during laboratory-scale PCB destruction, it has been shown that the SCWO technology has the potential to form high concentrations of PCDFs during PCB degradation in experiments below 450°C. It has been reported that emissions contain no oxides of nitrogen or acid gases such as hydrogen chloride or oxides of sulfur and that process residues consist of water and solids if the waste contains inorganic salts or organic compounds with halogens, sulfur or phosphorus. Limited information has been reported regarding potential concentrations of undestroyed chemicals. The process is designed so that emissions and residues can be captured for reprocessing if needed.

Release control and post-treatment: Currently, there is no specific information available regarding post-treatment requirements.

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[24] Vijgen J., 2009, Provisional POPs Technology Specification and Data Sheets for the Secretariat of the Basel Convention, Supercritical water oxidation (SCWO)

[25] See *UNEP, 2017*

[26] General Atomics, Industrial Supercritical Water Oxidation (iSCWO)

Energy requirements: Energy requirements are expected to be relatively high because of the combinations of high temperatures and pressures. It has been claimed, however, that as long as relatively high hydrocarbon content is present in the feed, no energy input is required to heat the feed to supercritical temperatures.

Material requirements: SCWO and subcritical water oxidation reaction vessels must be constructed of materials capable of resisting corrosion caused by halogen ions. Material corrosion can be severe at the temperatures and pressures used in the SCWO and subcritical water oxidation processes. In the past, the use of titanium alloys has been proposed to tackle this problem. Current vendors claim to have overcome this problem through the use of advanced materials and engineering designs.

Portability: The SCWO and subcritical water oxidation units are used in both fixed and portable configurations.

Health and safety: The temperatures and pressures used in SCWO and subcritical water oxidation processes require special safety precautions[27].

Capacity: Current SCWO demonstration units are capable of treating 500 kg/h, while full-scale units can be designed to treat up to 10,000 kg/h.

Other practical issues: Earlier designs were plagued by reliability, corrosion and plugging problems. Current vendors claim to have addressed these problems through the use of special reactor designs and corrosion-resistant materials.

State of commercialization: A full-scale SWCO commercial facility with the capacity to treat 2 tonnes of waste per day was installed in 2005 and is in operation in Japan. There are plants in commercial operation also in and Korea. In addition, the SCWO process has been approved for full-scale development and use in the chemical weapons destruction program of the United States. Several companies in the United States are working to commercialize supercritical reactors to destroy hazardous wastes. Widespread commercial application of SCWO technology requires a reactor design capable of resisting fouling and corrosion under supercritical conditions.

In Europe, Chematur Engineering AB of Sweden commercialized the SCWO technology for treatment of spent chemical catalysts to recover the precious metal, the AquaCat process. The unit has been built for Johnson Matthey in the UK. It is the only commercial SCWO unit in Europe and with its capacity of 3,000 l/h it is the largest SCWO unit in the world. Chematur's Super Critical Fluids technology was acquired by SCFI Group (Cork, Ireland) who are actively commercializing the Aqua Critox SCWO process for treatment of sludge, e.g. de-inking sludge and sewage sludge. Many long duration trials on these applications have been made and thanks to the high destruction efficiency of 99.9% + the solid residue after the SCWO process is well suited for recycling – in the case of de-inking sludge as paper filler and in the case of sewage sludge as phosphorus and coagulant. SCFI Group operates a 250 l/h Aqua Critox demonstration plant in Cork, Ireland.

Turbosystems Engineering (California, USA) is actively commercializing their patented transpiring wall SCWO reactor ("TWR") with a focus on renewable energy applications. The

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[27] See *Vijgen J., 2009*

TWR has been demonstrated to provide superior resistance to fouling and corrosion. The TWR is capable of operating at reaction temperatures in excess of 800°C, at pressures above or below the critical pressure of water, and has been demonstrated at a feedrate of 20 l/h.

Recently, most supercritical fluid technology has been confined to the laboratory since it is expensive and usable only on a comparatively small scale. This technology will enable commercial applications through reduction of the operation pressure, and subsequent drastic reduction in cost of the production equipment[28].

Summary:

- Specialized commercial plants operating in a number of developed countries.
- Remains under evaluation and demonstration for more general POPs applications.
- Is able to process low to medium volumes of hazardous wastes.
- Technology vendor with stable licensee arrangements that should be capable of competitive tendering worldwide.
- High level of complexity.

7. Cement kiln co-processing[29,30]

Cement kiln co-processing of hazardous wastes provides high temperatures, long residence time, surplus oxygen, good mixing and an alkaline environment, as well as efficient recovery of any energy and raw material substitutes in the hazardous waste.

Co-processing of hazardous wastes in cement kilns has been practiced for more than 30 years and is acknowledged to be feasible for sound hazardous waste treatment in both EU and US regulation, as well as in numerous other countries[31]. The US Environmental Protection Agency (EPA) has done numerous studies on the influence of co-processing hazardous wastes in cement kilns. Cement kiln operators in the US began recovering energy from organic waste materials, including hazardous chlorinated compounds, as early as 1974. That practice became commonplace by 1987 and since 1991 US cement kilns have used roughly 1,000,000 tonnes per year of hazardous waste as fuel substitute. Some of these kilns replace up to 100 % of their conventional fuels with waste-derived fuels.

Testing of cement kiln emissions for the presence of organic chemicals during the burning of hazardous materials has been undertaken since the 1970s, when the practice of co-processing hazardous wastes in cement kilns was first considered. Numerous tests around the world have demonstrated that there is essentially no difference in the emissions or the product quality when hazardous waste materials are used to replace the fuels and ingredients needed to produce cement clinker.

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[28] General Atomics, Industrial Supercritical Water Oxidation (iSCWO)

[29] UNEP, 2011, Technical guidelines: Technical guidelines on the environmentally sound co-processing of hazardous wastes in cement kilns

[30] See *UNEP, 2002, UNEP, 2017*

[31] Currently, about 40 % of the fuel used for klinker production in European cement kilns is substituted by alternative fuels like hazardous wastes.

Process description: Cement kilns typically consist of a long cylinder of 50–150 meters in length, inclined slightly from the horizontal (3-4% gradient), which is rotated at about 1-4 revolutions per minute. Raw materials such as limestone, silica, alumina and iron oxides are fed into the upper or "cold" end of the rotary kiln. The slope and rotation cause the materials to move toward the lower or "hot" end of the kiln. The kiln is fired at the lower end of the kiln, where material temperatures reach 1,400°C - 2,000°C. As the materials move through the kiln, they undergo drying and pyroprocessing reactions to form clinker.

Although the practice varies among individual plants, cement manufacture can consume significant quantities of wastes as fuel and non-fuel raw materials. This consumption reflects the process characteristics in clinker kilns, which ensure the complete breakdown of the raw materials into their component oxides and the recombination of the oxides into the clinker minerals. The essential process characteristics for the use of hazardous and other wastes, fed to the kiln via appropriate feed points, can be summarized as follows:

- Maximum temperatures of approximately 2,000°C (main firing system, flame temperature) in rotary kilns;
- Gas retention times of about 8 seconds at temperatures above 1,200°C in rotary kilns;
- Material temperatures of about 1,450°C in the sintering zone of rotary kilns;
- Oxidising gas atmosphere in rotary kilns;
- Gas retention time in the secondary firing system of more than 2 seconds at temperatures above 850°C; in the pre-calciner, the retention times are correspondingly longer and temperatures are higher;
- Solids temperatures of 850°C in the secondary firing system and/or the calciner;
- Uniform burnout conditions for load fluctuations due to the high temperatures at sufficiently long retention times;
- Destruction of organic pollutants because of high temperatures at sufficiently long retention times;
- Sorption of gaseous components such as HF, HCl, and SO_2 on alkaline reactants;
- High retention capacity for particle-bound heavy metals;
- Short retention times of exhaust gases in the temperature range known to lead to potential formation of PCDDs/PCDFs;
- Simultaneous material recycling and energy recovery through the complete use of fuel ashes as clinker components;
- Product-specific wastes are not generated due to a complete material use into the clinker matrix (although some cement plants dispose of CKD (Cement Kiln Dust) or bypass dust);
- Chemical-mineralogical incorporation and immobilisation of non-volatile heavy metals into the clinker matrix. Due to the large volumes of klinker produced, heavy metal contents remain below maximum permissible levels.

Cement kilns treating wastes may require kiln modifications. Adequate feed points should be selected according to the characteristics of the waste, including its physical, chemical and toxicological properties. For example, combustible toxic compounds found in some hazardous waste, such as halogenated organic substances, need to be completely destroyed through proper temperature and residence time. In preheater/precalciner kilns, hazardous waste should generally be fed through either the main or the secondary burners. Halides (e.g. chlorides, bromides and fluorides) have an impact on the quality of the cement so their presence must be limited.

Chlorine can be found in all raw materials used in cement manufacture, so total halogen (e.g. chlorine, bromine and fluorine) levels in the hazardous waste can be critical. However, if they are blended down sufficiently, cement kilns can treat highly chlorinated hazardous waste.

The potential feed point for supplying waste would be[32]:

- The main burner at the rotary kiln outlet end;
- A feed chute at the transition chamber at the rotary kiln inlet end (for lump fuel);
- Secondary burners to the riser duct;
- Precalciner burners to the precalciner;
- A feed chute to the precalciner/preheater (for lump fuel);
- A mid-kiln valve in the case of long wet and dry kilns (for lump fuel).

Liquid wastes are typically injected into the hot end of the kiln. Solid wastes may be introduced into the calcining zone at some facilities. This is mid-kiln for long kilns, and onto the feed shelf in the high-temperature section for preheater/precalciner kilns.

Solid wastes used as alternative raw materials are typically fed into the kiln system via the normal raw meal supply, the same as traditional raw materials. However materials containing components that can be volatilised at low temperatures (for example, solvents) should be fed into the high temperature zones of the kiln system. Wastes containing volatile organic and inorganic components should not be fed via the normal raw meal supply unless controlled test runs in the kiln, or adequate laboratory tests, have demonstrated that undesired stack emissions can be avoided.

Combustible toxic compounds found in some hazardous waste, such as halogenated organic substances, need to be destroyed through proper temperature and residence time. In preheater/precalciner kilns, hazardous waste should generally be fed through either the main or the secondary burners. Hazardous and other wastes fed through the main burner, where conditions will always be favorable, decompose under oxidising conditions at a flame temperature of >1800°C. Waste fed to a secondary burner, preheater or precalciner will be exposed to lower temperatures, though expected burning zone temperatures in the precalciner are typically >1000°C. The kiln should be operated in such a way that the gas resulting from the process is heated, after the last injection of combustion air, in a controlled and homogeneous fashion and even under the most unfavorable conditions, to a temperature of 850 °C for two seconds (cf. Directive 2000/76/EC). In the case of hazardous wastes with a content of more than 1% of halogenated organic substances (expressed as total chlorine), the temperature should be raised to 1100°C for at least two seconds. Under the United States TSCA, disposal of PCBs requires a temperature of 1200°C and 2 seconds retention time (at 3 % excess oxygen in the stack gas).

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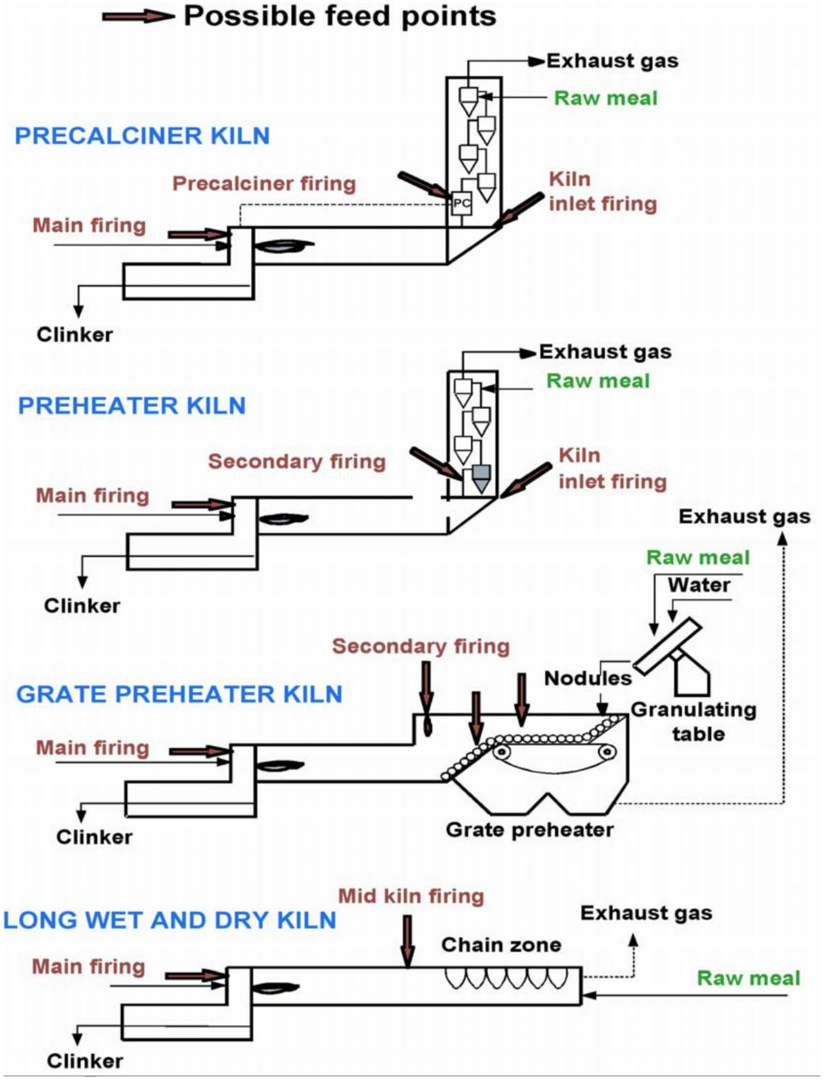
[32] See *UNEP, 2011, UNEP, 2017*

Typical waste feed points



For hazardous waste feeding into the kiln, the following should be conducted:

- To use the appropriate feed points to the kiln in terms of temperature and residence time depending on kiln design and kiln operation;
- To feed waste materials containing organic components that can be volatilized before the calcinic zone into the adequately high temperature zones of the kiln system;
- To operate in such a way that the gas resulting from the process is heated in a controlled and homogeneous fashion and even under the most unfavorable conditions to a temperature of 850°C for 2 seconds;
- To raise the temperature to 1100°C, if hazardous waste with a content of more than 1% of halogenated organic substances, expressed as total chlorine, is fed into the kiln;
- To feed wastes continuously and constantly;
- To stop feeding waste when appropriate temperatures and residence times are not maintained or cannot be reached (at start-ups or shutdowns of the kiln for instance), and whenever any emission limit value is exceeded.

The guidance on BAT/BEP developed by the Stockholm Convention relevant to Article 5 and Annex C on cement kiln firing hazardous waste should be used and applied to this technology[33].

Efficiency: A wide variety of hazardous wastes containing organic compounds, including aldehydes, esters, alcohols, ketones, phthalates, alcohol ethers, aromatic compounds, phenols, amines, amides, ethers, nitriles, freons and other halogenated organic compounds are commonly found in hazardous waste fuel mixtures used in the cement industry. More than 250 organic compounds have been approved for use in hazardous waste fuel in the US.

DREs greater than 99.99998% have been reported for PCBs in several countries. A facility should demonstrate its capability to destroy (through combustion) or remove (through settling in ductwork or air pollution control devices) at least 99.9999% of targeted POPs. Reported DE and DRE values for DDT are in the range of 99.9335-99.9998 % and 99.9984-99.9999%, respectively. Considering very high temperatures and long residency time found in state of the art cement kiln co-incineration facilities, it is expected that PCN (polychlorinated naphthalenes), PCP (pentachlorophenol) and HCBD (hexachlorobutadiene) would also be destroyed. Process operating constraints may become significant when certain compounds, for example circulating volatile elements such as chlorine, sulfur or alkalis, are present in excessive quantities[34]. Cement Kilns are recommended as high potential for applicability to HFCs destruction, including HFC-23[35].

Waste types: Virtually any organic compound can be destroyed at the minimum temperature of 1,400°C of a properly operating cement kiln. Cement kilns are capable of treating both liquid and solid wastes. Capacity to treat all POPs: Numerous tests around the world have demonstrated no difference in the emissions or the product quality when waste materials are used to replace the fuels and ingredients needed to produce cement clinker. Comprehensive emission studies have been performed when hazardous waste was introduced, and these have generally concluded that no significant differences could be measured between usages of the two fuels. In 1975 and 1977 carried out test burns with hazardous chlorinated hydrocarbons containing up to 46% chlorine in a wet cement kiln in Canada and concluded that "all starting materials, including 50 % PCBs, were completely destroyed to at least 99.98% efficiency in all cases" and emissions of high molecular weight chlorinated hydrocarbons were not detected.

Similar tests with chlorinated and fluorinated hydrocarbons conducted in a wet kiln in Sweden showed that the DRE of PCBs were better than 99.99998% and that there was no change in product quality or any influence on process conditions with a chlorine input up to 0.7 w% of the clinker production. Also, "no TEQ dioxins or furans could be detected". Viken and Waage (1980) carried out test burns in a wet kiln in Norway feeding 50 kg PCBs per hour, showing a DRE better than 99.9999% and no traces of PCBs in clinker or dusts could be detected and "PCDD and PCDF have not been detected". Benestad (1989) carried out studies in a dry preheater cement kiln in Norway in 1983 and 1987 and concluded that the "type of hazardous wastes used as a co-fuel" does not influence the emissions and that the destruction of PCBs were better than 99.9999%. "0.2 ng PCDD/Fs TEQ/m^3 and 0.1 ng PCDD/Fs TEQ/m^3 were measured

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[33] Stockholm Convention, Best Available Techniques (BAT)

[34] See *UNEP, 2017*

[35] TEAP Report, 2018, Volume 2: Decision XXIX/4 TEAP Task Force Report on Destruction Technologies for Controlled Substances

when feeding hydrocarbon waste (fatty acid esters, solvents and paint residues) and PCBs-waste respectively"[36].

Seen from a process technical and chemistry viewpoint it is easier to dispose liquid POPs like PCBs contaminated oils than solid materials. Independent of the state of the material, pre-treatment, analysis and control, and cautious feeding of POPs material is necessary. The chlorine tolerance of the process needs to be known.

Capacity to treat hazardous wastes: Cement kilns are a versatile alternative for the management of a wide variety of hazardous wastes. The raw materials used to produce cement often contain trace quantities of virtually every natural element, including alkali chlorides and sulfates; heavy metals, such as lead, cadmium, chromium and arsenic; and organic materials. Many of these constituents are also contained in fossil fuels, such as coal, oil and petroleum coke, and in the water used to prepare slurry for wet process kilns.

Materials present in the feed, fuels or hazardous waste introduced into the kiln become part of the cement product (klinker) and a waste material known as cement-kiln dust is formed, or they are converted to other forms within the kiln. With few exceptions, materials introduced into cement kilns will be oxidized and stabilized, requiring no further treatment.

Many cement kilns burning hazardous waste as fuel have chosen not to burn PCBs wastes for reasons of perception, bad reputation and fear for market implications.

Pre-treatment: Some waste categories have to be pre-treated in order to comply with the technical specifications of cement production and to guarantee that environmental standards are met.

Pre-treatment in a mixing station can involve:

- Thermal desorption of solid wastes;
- Homogenization of solid and liquid wastes through drying, shredding, blending, mixing and grinding;
- Volume reduction; and
- Blending.

The mixing station with its analytical lab has also to ensure correct chemical properties of the alternative fuel to be fed into the cement kiln.

High concentration POPs should always be fed to the high temperature burning zone, i.e. main burner or pre-calciner burner. The method of introducing liquid and solid hazardous waste into the kiln is a key factor to the complete consumption of the waste during the combustion of the primary fuel. Liquid hazardous waste is either injected separately or blended with the primary fuel. Solid waste is mixed and burned along with the primary fuel. Fuel and wastes fed through the main burner will be decomposed under oxidizing conditions in the primary flame burning zone at temperatures up to 2,000°C and long residence times. Fuel and waste fed to the secondary burner, pre-heater or pre-calciner will be burnt at temperatures between 900°C and 1,200°C. The US TSCA (Toxic Substances Control Act) PCBs incineration criteria require a temperature of 1,200°C and 2 seconds retention time at 3% oxygen; the EU Directive 2000/76/EU requires a temperature of 850°C for at least 2 seconds for the incineration of

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[36] See *UNEP, 2002*

nonchlorinated hazardous waste and 1,100°C and 2 seconds retention time for organic substances containing more than 1% halogens at 2% oxygen[37].

Emissions and residues: Cement kiln co-incineration of hazardous wastes is listed as an industrial source category that has the potential for comparatively high formation and release of the unintentionally formed POPs listed in Annex C to the Stockholm Convention. Emissions may include, *inter alia*, nitrogen oxides, carbon monoxide, sulfur dioxide and other oxides of sulfur, metals and their compounds, hydrogen chloride, hydrogen fluoride, ammonia, PCDDs, PCDFs, benzene, toluene, xylene, polycyclic aromatic hydrocarbons, chlorobenzenes and PCBs and PCN. It should be noted that cement kilns can comply with PCDD and PCDF air emission levels below 0.1 ng TEQ/Nm^3 although waste with high chlorine levels should be diluted and fed together with other wastes to avoid adversely affecting emission levels, particularly in wet and (long) dry kilns. Some cement plants produce cement kiln dusts (CKD) which cannot be reintroduced to the process due to process or quality constraints; usually the CKD are reused as a mineral-substitute but some plants landfill their CKDs. Potential contamination needs to be checked. Modern plants usually comply with emission limit values with good margins. Plants which co-process hazardous waste must comply with the stringent emission limit values for hazardous waste incinerators.

Release control and post-treatment: Process gases must be treated to remove cement kiln dust and organic compounds, sulfur dioxide and nitrogen oxide; they must also be heated so that the formation of PCDDs and PCDFs is minimized. Treatments include the use of preheaters, electrostatic precipitators, fabric filters and activated carbon filters. Recovered cement kiln dusts should be put back into kilns to the maximum extent practicable, while the remainder may require disposal in a specially engineered landfill or permanent storage in an underground mine or formation.

Energy requirements: For new facilities and major upgrades using dry process kiln with multistage preheating and precalcination, the BAT-associated energy consumption is 2,900-3,200 MJ/tonne clinker under normal (excluding, e.g. start-ups and shutdowns) and optimised operational conditions (not applying to facilities producing special cement or white cement clinker that require significantly higher process temperatures due to product specifications). The production capacity has an influence on the energy demand, with higher capacities providing energy savings and smaller capacities requiring more energy. Energy consumption also depends on the number of cyclone preheater stages, with more cyclone preheater stages leading to lower energy consumption of the kiln process. The appropriate number of cyclone preheater stages is mainly determined by the moisture content of raw materials.

Material requirements: Cement manufacturing requires large amounts of materials, including limestone, silica, alumina, iron oxides and gypsum.

Cement kilns produces from a few tonnes cement clinker per hour and up to several hundred tonnes per hour, which means that the fuel-firing requirements vary from a few tonnes to several tens of tonnes of fuel per hour. Yearly capacities vary from a few thousand to more than 10 million tonnes per year (in Thailand). Usually fine coal is used as the primary fuel.

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[37] See *UNEP, 2002*

POPs throughput: [POPs waste/total waste in %]: The waste throughput will depend on the total mass flow of fuel: there are kilns which are licensed to substitute 100 % of its conventional fuel with organic hazardous wastes. For POPs waste a responsible throughput from a few tens of kg per hour to several thousand kg per hour can be expected. As rule of thumb, chlorine should usually be limited to 350 to 500 g/t cement clinker for a kiln without by-pass and 400 to 750 g/t for a kiln with by-pass. Important is that the process owner needs to know the chlorine tolerance of the process in question.

Portability: Cement kilns are available only in fixed configurations.

Health and safety: Treatment of wastes in cement kilns can be regarded as relatively safe provided that kilns are properly designed and operated.

Capacity: Cement kilns that co-incinerate waste as fuel must normally not meet more than 40 % of their heat requirements with hazardous waste. It has been noted, however, that cement kilns with high throughput can potentially treat significant quantities of waste.

State of commercialization: Cement kilns in the United States, some European countries and a number of developing countries have been and are used to treat wastes contaminated with.

Limitations: The feasibility of a cement kiln for treatment of POPs should be investigated by experts on a case by case basis. There are kilns which are not recommended to use for POPs treatment, for example vertical shaft kilns or kilns with improper environmental performance. The chlorine tolerance of a kiln differs widely due to process constraints, but as rule of thumb, chlorine should usually be limited to 350 to 500 g/t cement clinker for a kiln without by-pass and 400 to 750 g/t for a kin with by-pass[38].

Costs: The reason that cement plants are taking waste is usually to save costs. In general the cement plants are cheaper than other technologies, but this may not be the case with POPs because the monitoring and control requirements will add to the costs significantly. If a plant decides to go in hazardous waste co-processing, the owner will do these investments themselves. The listed experience in Vietnam for example and the prices offered by the cement plant need to be competitive to the market, independent of the investment.

Summary:

- Commercial application in developed countries and demonstrations in developing countries.
- Generally limited to relatively modern rotary kiln units with overall BAT/BEP environmental performance equipped with appropriate POPs waste handling/ injection infrastructure as well as monitoring capacity.
- Application requires case by case assessment and performance demonstration.
- Shifting to co-incineration will need upfront investments into mixing station and off-gas monitoring.

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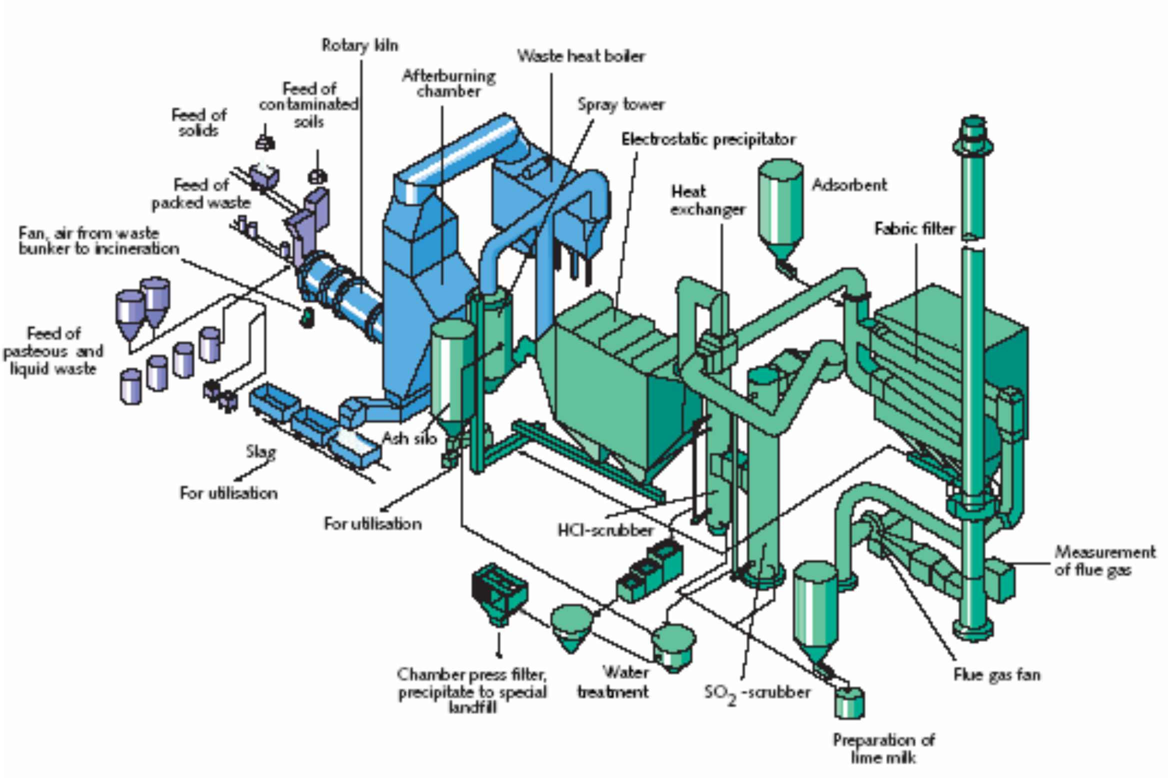
[38] See *UNEP, 2002*

8. Hazardous waste incineration[39]

Process description: Hazardous waste incineration uses controlled flame combustion to treat organic contaminants, mainly in rotary kilns. Typically, a process for treatment involves heating to a temperature greater than 850° C or, if the waste contains more than 1% of halogenated organic substances expressed as total chlorine, to a temperature greater than 1,100°C, with a residence time greater than two seconds. Dedicated hazardous waste incinerators are available in a number of configurations, including rotary kiln incinerators and static ovens (for liquids with low contamination). High-efficiency boilers and lightweight aggregate kilns are also used for the co-incineration of hazardous wastes.

The guidance on BAT/BEP developed by the Stockholm Convention relevant to Article 5 and Annex C for waste incinerator should be used and applied to this technology[40].

Process diagram (Example: Incineration plant in Finland)[41]:



Efficiency:

Destruction and Removal Efficiencies (DREs) greater than 99.9999 % have been reported for treatment of PCBs, PCDDs and PCDFs, chlordane and HCB. Destruction Efficiencies (DEs) greater than 99.999 % and DREs greater than 99.9999 % have been reported for aldrin, endrin, HCH, DDT and PFOS (Ministry of the Environment of Japan, 2004 and 2013). In 2016

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[39] See *UNEP, 2002 & UNEP, 2017*

[40] Stockholm Convention, Best Available Techniques (BAT)

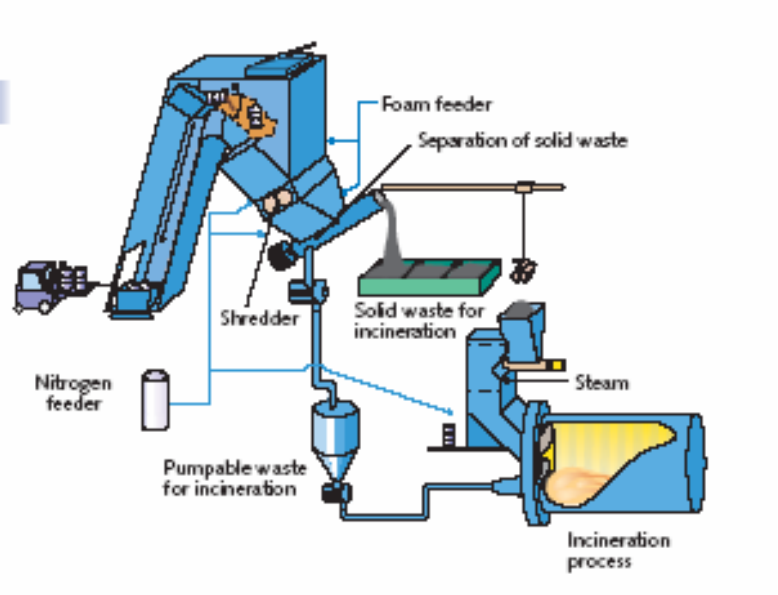
[41] UNEP, 2004b. POPs Technology Specification Data Sheet: Hazardous Waste Incineration

Yamamoto reported DE and DRE for PCN at 99.9974 % and 99.9995 %, respectively. State-of-the-art incineration reaches destruction rates of more than 99.9 % for HCBD and PCP and between 99.32 % and 99.96 % for PCNs (Germany Federal Environment Agency, 2015).

Waste types: Hazardous waste incinerators are capable of treating wastes including wastes consisting of, containing or contaminated with POPs. Incinerators can be designed to accept wastes in any concentration or physical form, i.e., as gases, liquids, solids, sludges or slurries. For the incineration process there is no difference between treating POPs or other kinds of hazardous wastes, which also can content higher concentrations of sulphur, chlorine, bromine, fluorine or heavy metals. Starting with checking the inventory, an analysis must be made to define the correct packaging and weight of the single drums filled with POPs in different concentrations to be added to the daily incineration programme in order to avoid incinerator emission peaks. Thereby, no difference in the continuous emission monitoring with and without POPs incineration can be seen. One reason is the big buffer capacity in the flue gas treatment installations.

Pre-treatment: Depending upon the configuration, pre-treatment requirements may include blending and size reduction of wastes.

Example: Pre-treatment in Finland



For polystyrene foam (EPS and XPS) wastes containing HBCD, a series of steps can be applied to separate HBCD from polystyrene and subsequently destroy HBCD in hazardous waste incinerators. The relevant pre-treatments operations include volume reduction, size reduction, dissolution, sedimentation, and distillation. In the case of XPS waste containing HBCD and which may also contain ozone depleting substances controlled by the Montreal Protocol on

Substances That Deplete the Ozone Layer[42], measures should be taken to prevent the release of ODS to the environment during these pre-treatment operations.

Emissions and residues: very low PCDD and PCDF discharges to water. PCDDs and PCDFs are mainly found in fly ash and salt, and to some extent in bottom ash and scrubber water sludge.

Emissions include carbon monoxide, carbon dioxide, HCB, hydrogen chloride, particulates, PCDDs, PCDFs and PCBs, heavy metals and water vapours. Incinerators applying BAT that, *inter alia*, are designed to operate at high temperatures to destroy PCDDs and PCDFs, prevent the re-formation of PCDDs and PCDFs, and to remove PCDD and PCDF traces (e.g. with the use of activated carbon filters), have led to very low PCDD and PCDF emissions to air and discharges to water. In residues, PCDDs and PCDFs are mainly found in fly ash and salt, and to some extent in bottom ash and scrubber water sludge. Levels of PCDD/Fs in fly ash from hazardous waste incinerators can be in the range from 0.0002 to 124.5 ng TEQ/g[43].

Generated waste (% of input waste): ca. 30% (ashes, filter dust and active carbon).

Deposited waste at landfill (% of input waste): 28.8 % (consisting of ashes, filter dust and active carbon) is deposited at special landfill (Saltmines) with max. dioxin content of 33 ng TEQ/kg for ashes and 1,200 ng TEQ/kg filter dust (Recovery operation R5)[44].

Release control and post-treatment:
Process gases may require treatment to remove hydrogen chloride and particulate matter and to prevent the formation of, and remove unintentionally produced POPs (sulphur and nitrogen oxides, heavy metals and organic micro pollutants such as PAHs, like carbon monoxide, are being used as an indicator of combustion efficiency). This can be achieved through a combination of types of post-treatments, including the use of cyclones and multi-cyclones, electrostatic filters, static bed filters, scrubbers, selective catalytic reduction, rapid quenching systems and carbon adsorption. Depending upon their characteristics, bottom and fly ashes may require disposal within a specially engineered landfill or permanent storage in underground mines and formations.

Sampling requirements/facilities: Continuous flue gas monitoring according to air pollution regulations and drainage water sampling. In some cases samples from the stack gas are taken in a discontinuous mode and analysed by independent laboratories. In case of POPs/PTS (Persistent Toxic Substances) releases it is possible to return components to the process. Some facilities monitor their gaseous releases monthly/annually to verify compliance with air discharge permit and some facilities hold and test solids and effluents prior to discharge for total organic chlorine (TOCl), total organic carbon (TOC), pH, temperature, turbidity, and heavy metals concentration.

Process gases may require treatment to remove hydrogen chloride and particulate matter and to prevent the formation of, and remove unintentionally produced, POPs (note: sulphur and nitrogen oxides, heavy metals and organic micro pollutants such as PAHs, like carbon monoxide, are being used as an indicator of combustion efficiency). This can be achieved through a combination of types of post-treatments, including the use of cyclones and multi-cyclones, electrostatic filters, static bed filters, scrubbers, selective catalytic reduction, rapid quenching

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[42] Montreal Protocol on Substances That Deplete the Ozone Layer

[43] See *UNEP, 2017*

[44] See *UNEP, 2002*

systems and carbon adsorption. Depending upon their characteristics, bottom and fly ashes may require disposal within a specially engineered landfill or permanent storage in underground mines and formations.

Resource needs: Hazardous waste incinerators can treat between 30,000 and 100,000 t/year. Full-Scale plants example Germany[45]: 2 rotary kilns with a total capacity of 110,000 t/year for solid, fluid, and paste, gaseous and in drums packed hazardous wastes.

Portable Plants: one is applied in Estonia with an annual capacity of 1,620 tonnes working continuously. The reconstruction works were finished at the beginning of 2006 and now the plant measures up to legislation in Estonia and EU directive 2000/76/EC on the incineration of waste. In the plant, at the same time, it is possible to treat waste in three states: liquid, solid, jellied. Very different kinds of hazardous wastes are treated: waste from colours/coatings and lacquers; medicines and infectious waste, contaminated packages and other materials; oil filters; contaminated soil, chemicals, PCBs-oil, pesticides etc.

In Latvia a container-based Incineration system (CIS) with a capacity of 2,000-4,000 t/year depending on calorific value of waste. Waste can contain to 2.5% sulphur and to 10% halogen (mostly chlorine).

POPs throughput : [POPs waste/total waste in %] max 10% chlorines or halogens. There are also specific hazardous waste treatment plants that can deal with high chlorine contents. Most of them are integrated in the plants of the chemical industry recycling their own waste and are often not accepting production from the market. However there are a number of plants accepting highly chlorinated waste from the external market. Treatment of solid and liquid waste is possible. Some are treating liquid organic high Cl-containing waste. Experiences have been made with liquid POPs waste such as PCB-oils (liquid) and other highly chlorinated non-POPs waste like methylene-chloride, perchloorethylene, trichloorethylene. For example, PCBs have been treated and the chlorine is recuperated as the product HCl and can be used in a wide variety of applications. High processing temperature (>1,450°C) guarantees destruction of all PCBs.
Energy requirements: The amount of combustion fuel required will depend upon the composition and calorific value of the waste and also upon the flue gas treatment technologies applied.

Power requirements: 170 KWh/t. The installation produces in one turbine the energy itself. One part is supplied to the public electricity grid, being ca. 15% of the generated energy.

Fuel volumes: Only 4.4 kg/t combustion oil is used during heating up of an installation after standstill. Normally the installation runs completely by the heat of the waste burnt.

Material requirements: Material requirements include cooling water and lime or another suitable material for removal of acid gases and other pollutants like active carbon.

Water requirements: 1.7 m^3/t/year, for example in Germany a plant with 2 rotary kiln with a total capacity of 110 000 t/year taken per year draws the water from an own water supply well;

Reagents volumes: 40 kg/t of 50 % NaOH is used for the neutralisation of acid gases in the wet scrubber, the exact amount is very much dependent on the halogen and sulfur content of the wastes;

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[45] See *UNEP, 2004b*

Activated carbon/chalk mixture is 1.5 kg/t (in the last step of the gas cleaning system for removing traces of dioxins and mercury.

Laboratory requirements: A broad variety of spectroscopic, colorimetric and chromatographic techniques are used for monitoring of emissions , such as gas chromatography (GC), mass spectrometry (MS), GC/MS, inductively coupled plasma spectrometry (ICP), ion chromatography (IC), poly urethane foam (PUF) air monitoring, infrared (IR) spectroscopy, standard dust monitors, fly ash tests, slag tests, wipe tests, titrimetric methods, and mass balance analysis.

Utilities required for hazardous waste treatment

(Data are general numbers for 2013, but not specifically for highly concentrated pesticides waste)

Utility	**Units**	**Quantity required per tonne of waste input**	**Quantity required per year (110,000 tonnes full-scale plant)**
Electricity	kWh	170	18,700,000
Electricity produced and supplied to public grid	MWh		1,700
(50 %) NaOH	kg	40	4,400,000
CO_2 production	kg	820	90,000,000
Oil	kg	4	440,000
Active carbon /calcium hydroxide mix	kg	1.4	150,000
Cooling and scrubbing water (own supply well)	m^3	1.7	187,000
Slag production	kg	215	23,600,000
Filter dust and spray dryer residue	kg	46	5,100,000
Processing rate	kg /min		
	t/month		9,170
	t/year		110,000

- Oil consumption: only used for start-up of the installation after standstill, otherwise the installation runs automatically only with heat generated by the waste burning
- NaOH is only used to neutralize acid gas in the wet scrubber, strongly depending on halogen and sulfur content of the waste

- Active carbon /calcium mix is occurring in the last step of the flue gas cleaning (for traces of dioxine and mercury)[46]

Portability: Hazardous waste incinerators are available in both portable and fixed units.

Health and safety: Health and safety hazards include those associated with operations involving high temperatures. Plant workers have been required to be trained in hazardous waste operations.

Capacity: Hazardous waste incinerators can treat between 30,000 and 100,000 tonnes of waste per year.

Other practical issues: it is an industrial process relying on quality management and a skilled workforce and a market able to deliver sufficient amounts to be incinerated

Costs: Rough calculation of a new plant in a country based on existing standards in Germany: - throughput 2 x 50,000 t/year treating solid, liquid, pastes, drums - thermal capacity (with boiler) 2 x 22 MW - buffer capacity for waste 5 days would require investment ca. 50 mln US$ plus 85 people staff[47].

State of commercialization: There is a long history of experience with hazardous waste incineration.

Summary:

- Proven commercial application in developed countries.
- High capital and operating costs.
- Sophisticated emission controls and monitoring required.
- Economies of scale >30,000 t/year generally required for development with broad application to hazardous organic wastes generally.
- Mobile/semi-mobile 2-5,000 t/year capacity available but with cost premium and potential environmental performance penalties.

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[46] See *UNEP, 2004b*

[47] See *UNEP, 2004b*

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