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# GUIDELINES FOR PCBs, PCB-CONTAINING EQUIPMENT AND WASTE DISPOSAL



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## 1. INTRODUCTION

The main purpose of these guidelines are to provide the information about the existing technologies available for the disposal of the PCBs. It also explains about the chemical mechanisms and process principle involved in these technologies. It also allows one to select and evaluate these disposal technologies for PCBs. Since these technologies are cost effective, the cost figures have not been reported. This selection process is a part of UNIDO/GEF project “Environmentally sound management and final disposal of PCBs in India”.

## 2. INTERNATIONAL STANDARDS FOR THE DISPOSAL OF POPs

### 2.1. STOCKHOLM CONVENTION BAT / BEP

The definition of disposal in compliance of Article 6.1(d)(ii) of the Stockholm Convention on Persistent Organic Chemicals is that Stockpiles of POPs and waste contaminated by POPs must be

- *Disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of persistent organic pollutants*
- *or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option or the persistent organic pollutant content is low,*
- *taking into account international rules, standards, and guidelines,... and relevant global and regional regimes governing the management of hazardous wastes”*

Article 5 and Annex of the Stockholm Convention establishes that measures shall be established to reduce or eliminate releases from unintentional production.

More specifically, Annex V establishes that the use of best available techniques for new sources must be promoted and required; and that in any case, “*the requirement to use best available techniques for new sources in the categories listed in Part II of that Annex shall be phased in as soon as practicable but no later than four years after the*

*entry into force of the Convention for that Party. For the identified categories, Parties shall promote the use of best environmental practices. When applying best available techniques and best environmental practices, Parties should take into consideration the general guidance on prevention and release reduction measures in that Annex and guidelines on best available techniques and best environmental practices to be adopted by decision of the Conference of the Parties;”*

The same annex provides also a definition for BAT and BEP, techniques and sources as following:

- (i) "Best available techniques" means the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for release limitations designed to prevent and, where that is not practicable, generally to reduce releases of chemicals listed in Part I of Annex C and their impact on the environment as a whole. In this regard:*
- (ii) "Techniques" includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;*
- (iii) "Available" techniques means those techniques that are accessible to the operator and that are developed on a scale that allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages; and*
- (iv) "Best" means most effective in achieving a high general level of protection of the environment as a whole;*
- (v) "Best environmental practices" means the application of the most appropriate combination of environmental control measures and strategies;*
- (vi) "New source" means any source of which the construction or substantial modification is commenced at least one year after the date of:*
  - a. Entry into force of this Convention for the Party concerned; or*
  - b. Entry into force for the Party concerned of an amendment to Annex C where the source becomes subject to the provisions of this Convention only by virtue of that amendment.”*

Guidance on BAT and BEP for disposal of PCBs is provided under the “*Guidelines on best available techniques and provisional guidance on best environmental practices European Union BAT / BEP*”

Of particular relevance are:

- Section V, Part II Source Category (a): waste incinerators
- Section V, Part II Part II Source category (b): Cement kilns firing hazardous waste

It should be noted that the BAT/BEP guidelines do not differentiate among “combustion” or “non-combustion” technologies. The presence or absence of a combustion process is not considered a relevant criterion for selecting or discarding a technology. However, the whole Section II of the Guideline discusses how alternatives should be evaluated in selecting a technology. The Stockholm Convention requires that a sound assessment of the alternatives should be carried out, including in the assessment also the technologies that, due to their specific and intrinsic features, ensure that the emission of UP-POPs is kept at a minimum or even completely avoided. This concept is well described in the following sentence extracted from section II of the BAT/BEP guidelines:

*“When a Party requires the application of best available techniques for a proposed new source of chemicals listed in Annex C, decision makers are encouraged to assure that consideration is also given to alternatives that avoid the formation and release of such chemicals. In doing this, they should undertake a comparison of the proposed process, the available alternatives and the applicable legislation using what might be termed a “checklist approach”, keeping in mind the overall sustainable development context and taking fully into account environmental, health, safety and socio-economic factors.”*

*“A proposed alternative should be given priority consideration over other options, including the originally proposed facility, if, based on the comparative evaluation described in subsection 3 above, and using relevant considerations and criteria from Convention Annex F and Annex C, an identified, available alternative is determined to:*

- *Avoid the formation and release of chemicals listed in Annex C;*
- *Have similar usefulness;*

- *Fit comparatively well within a country's sustainable development plans, taking into account effective integration of social, economic, environmental, health and safety factors."*

On the selection of alternatives, a recent advisory document drafted by STAP remarks that the *"policy of GEF is currently not to impose more restrictive requirements on developing countries and Countries with Economy in Transition than are being applied in developed countries."*

In the selection of alternatives it is also crucial to recognize that disposal is only part of the POPs management process, and that the comparison of alternative technologies must take into account, by means of formal evaluation instruments like EIA, the site features where the disposal facility has to be established.

## 2.2. BASAL CONVENTION

The Basel Guidelines, as periodically amended and adopted by the Convention constitute basic guidance and minimum standards applied to POPs stockpiles and waste disposal technology used in GEF funded projects. Of particular relevance to the disposal of PCBs are the following guidelines documents, available under the Basel Convention website

- Technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with polychlorinated d biphenyls (PCBs), polychlorinated terphenyls (PCTs) or polybrominated biphenyls (PBBs); Updated general technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (POPs).
- Technical guidelines on the environmentally sound co-processing of hazardous wastes in cement kilns (adopted at COP10)
- Technical guidelines on the environmentally sound management of wastes containing or contaminated with unintentionally produced PCDDs, PCDFs, HCB or PCBs

## 2.3. EUROPEAN UNION BAT / BEP

The main purpose of the EU was to provide guidance by BREF documents that is, BAT and BEP documents. The documents analyse various technologies and consider

several sectors namely waste water and waste gas treatment in chemical sector, Waste incineration, Waste treatment industries, keeping the prime focus on the disposal of PCBs.

### **3. INDIAN LEGISLATIVE FOR THE DISPOSAL OF HAZARDOUS WASTE AND POPs**

#### **3.1. PERMITTING AND ENVIRONMENTAL IMPACT ASSESSMENT**

In India, the State Pollution Control Board is in charge of issuing authorization for the establishment and operation of facilities for the disposal of hazardous waste (rule 5 of the Hazardous Waste Rules, 2008). The owner of the facility shall submit an application in compliance with Form I of the Hazardous Waste Rules, 2008. A disposal facility conforming to the internationally benchmarked Environmental Assessment (EA) shall be financially funded by GEF. And an Environmental Management Plan (EMP) for the same shall be implemented. EMP shall include regular monitoring and reporting on pollutant emission at the source, regular environmental monitoring and reporting, periodical assessment of the destruction efficiency (DE) and destruction and removal efficiency (DRE), safety at work and personal protective equipment.

### **4. CRITERIA FOR EVALUATING PCBs DISPOSAL EFFICIENCY**

#### **4.1. DE AND DRE**

Destruction Efficiency (DE) and the Destruction and Removal Efficiency (DRE) are the two key parameters to be measured for evaluating the destruction efficiency of the disposal technologies.

DE take into account the overall destruction efficiency, including the residues of the hazardous substance in all the process streams. It is defined as the total input mass of a chemical into a process, minus the mass of the chemical in all products, by-products and environmental releases, divided by the input mass, multiplied by 100 (to be shown as a percentage).

DE for PCDD/F and PCB will be measured in term of the sum of PCB + PCDD/F expressed as Toxicity Equivalent (WHO TEq) mass<sup>4</sup>. Destruction Efficiency (DE) for PCBs and PCDD/Fs  $(IN-OUT/IN)*100$ , calculated as TEQ in the below formula should not be less than 99.99%.

DE calculated as TEQ



$$IN = W_{PCB(TEQ)} + W_{PCDD/F(TEQ)}$$

$$OUT = \int_{t=0}^{t=end} Q_s (CS_{PCB+TCDD/F(TEQ)}) + \int_{t=0}^{t=end} Q_{BA} (CBA_{PCB+TCDD/F(TEQ)}) + \int_{t=0}^{t=end} Q_{FA} (CFA_{PCB+TCDD/F(TEQ)}) + \int_{t=0}^{t=end} Q_{SL} (CSL_{PCB+TCDD/F(TEQ)}) + M_{AC} (CAC_{PCB+TCDD/F(TEQ)})$$

DE for specific substance (X):

$$IN = W_X$$

$$OUT = \int_{t=0}^{t=end} Q_s CS_X + \int_{t=0}^{t=end} Q_{BA} CBA_X + \int_{t=0}^{t=end} Q_{FA} CFA_X + \int_{t=0}^{t=end} Q_{SL} CSL_X + \int_{t=0}^{t=end} Q_{AC} CAC_X$$

Where:  $W_{pcb}$ : mass weight of the PCB input,  $t=0$ : beginning of the waste feeding;  $t=end$ : end of the trial burn test;  $Q_s$ : Volumetric flow at the stack gas,  $Nm^3/h$ ;  $C_s$ : Concentration in the stack gas,  $ng/Nm^3$ ;  $C_{BA}$ : Concentration in the bottom ashes,  $ng/g$ ;  $C_{FA}$ : Concentration in the flying ashes,  $ng/g$ ;  $Q_{BA}$ : mass flow of the bottom ashes ( $kg/h$ );  $Q_{FA}$ : mass flow of the fly ashes ( $kg/h$ );  $M_{AC}$ : overall weight of the activated carbon pack. Oxygen reference value at the stack 11%.

DRE is defined as the total input mass of a chemical into a process, minus the mass of the chemical into exhaust gas, divided by the input mass, multiplied by 100 (to be shown as a percentage). Calculations of DE and DRE should use half the value of the detection limit of the method employed for any tests that result in “not detected”. Destruction and removal efficiency should be not less than 99.9999%.

#### 4.2. INFLUENCE OF THE PRETREATMENT ON DE AND DRE

The PCBs released during storage or pretreatment (measured or estimated) should be included in the calculation of DE and DRE. The final disposal efficiency (DE) of the whole process is therefore governed by the amount of PCB still present on the treated materials or released during the opening of PCBs equipment, which would comparably be much greater than the release with exhaust gases or the untreated PCBs after dehalogenation. Although the evaluation of DRE usually only quantifies the POPs concentration in the exhaust gases released from the stack during normal

operation, there could be fugitive emissions which are not considered; And this could lead to a significant increase in DRE when properly evaluated.

Practically, this means that proper countermeasure aimed at avoiding any release during the pre-treatment stage will ensure a significant increase in the actual DE and DRE; This increase would be at a cost which is often a fraction of the cost required to adopt sophisticated technologies for the reduction of emission at the stack.

#### 4.3. SHORTCOMINGS OF THE DE AND DRE APPROACH

The shortcomings of the DE and DRE approach are as follows:

- a. The concentration of POPs at the output stream is not linearly related to concentration of the POPs in the input stream. In case of incineration, the POPs released in the stack are lower due to the fact that the POPs are released during the combustion of the clean fuel. Therefore the treatment of low concentration POPs would result in higher DE and DRE.
- b. The value of DE and DRE depends upon the detective limit of the method adopted.
- c. DE and DRE do not provide the information of transformation of PCBs to other POPs. Therefore a thorough knowledge of the disposal method for POP is necessary.
- d. DE and DRE do not provide the information about the mass of pollutant released to the environment.
- e. The DE and DRE are measured by carrying out the test under the operation condition of the plant and test are carried under range of the operational condition. The environmental management plan should evaluate the measurement of test atleast once in a year.

#### 5. DISPOSAL TECHNOLOGIES AVAILABLE FOR PCBs

A few technologies, demonstrated in GEF for the disposal or decontamination of PCBs containing equipment and oils are as follows:

- Metallic Sodium dehalogenation
- Continuous Dehalogenation Process (A-PEG based)
- Incineration
- Thermal Desorption
- Co-incineration in cement kiln

- Decontamination of equipment with solvent washing

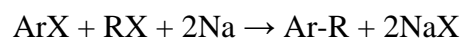
In addition to the above technologies, the following, have been included:

- Plasma
- Hydrodehalogenation

## 5.1. CHEMICAL DESTRUCTION OF PCBs

### 5.1.1. METALLIC SODIUM DEHALOGENATION PROCESSES

The general representation of the Wurtz-Fittig reaction is:



The effectiveness of the destruction/reaction process is based on the formation of sodium compounds with bonding enthalpies that are higher than those between the non-sodium ions and the stripped ion. These technologies may be adopted for the decontamination of transformer oil in a closed loop decontamination processes, or for the decontamination of PCBs contaminated oils. The metallic sodium dehalogenation technologies usually are not suitable for the decontamination of contaminated soils and wastes; however in some cases the metallic sodium process has been used for the dehalogenation of the oily fraction of landfill leachate or of fluorescent light ballast waste and capacitors.

Sodium is a reactive metal which reacts violently with water to give hydrogen gas, creating a potential fire hazard; Hence processes using metallic sodium usually requires degassing and dewatering of the media to be treated in order to avoid unwanted exothermic reactions. An inert gas (nitrogen or argon) is required for filling the head space of the reactors. The residues from the treatment process include sodium salts and various aromatic, non-halogenated hydrocarbons. Under pilot- and full-scale conditions, the organic byproducts are either combusted or recovered following refinement for appropriate post-treatment uses (e.g., energy recovery, reuse as dielectric fluids). The inorganic byproducts (together with the excess sodium added initially to the system) must be recovered and disposed of in an appropriate manner.

The introduction of metallic sodium into a PCB oil leads to a reaction whose rate is dependent on the metal-oil interface. As the rate of reaction between the solid metal

and the PCB-containing oils depends on the extent of this interface, the finer the metal particles, the faster will be the reaction.

Secondary reactions can occur when PCBs react with metallic sodium. During the dechlorination step, the intermediate chlorinated molecules can polymerize and lead to the formation of a solid (polymer) containing chlorine. This product can no longer be dechlorinated and settles out of the reaction as a solid.

In general, sodium dispersions proposed today are extremely fine and resemble emulsions, having a high metal surface area. The dispersion is used at a temperature which is above that of the melting point of the sodium, i.e., 98°C (normally in the range 110°C – 180°C), and at atmospheric pressure. Being liquid, the metal surface can be renewed continuously. In this way a reasonable reaction rate can be achieved, thereby decreasing the cost of the decontamination process.

#### 5.1.2. APEG DEHALOGENATION PROCESSES (GLYCOLATE/ALKALINE POLYETHYLENE GLYCOL)

Glycolate dehalogenation makes use of a chemical reagent called APEG. APEG consists of two parts: an alkali metal hydroxide (the “A” in APEG) and polyethylene glycol (PEG). The metal hydroxide that has been most widely used for this reagent preparation is potassium hydroxide (KOH) in conjunction with polyethylene glycol (PEG) (typically, average molecular weight of 400) to form a polymeric alkoxide referred to as KPEG; Sodium hydroxide has also been used for this process.

The process consists of mixing and heating the contaminated media with the APEG reagent. During heating, the alkali metal hydroxide reacts with the halogen from the contaminant to form a non-toxic salt; and the PEG takes the location in the PCB molecule formerly occupied by the halogen making it less hazardous. Process can be operated in batch or continuous mode. The concentrations of PCBs that have been treated are reported to be as high as 45,000 ppm. Concentrations were reduced to less than 2 ppm per individual PCB congener. PCDDs and PCDFs have been treated to nondetectable levels at part per trillion sensitivity. In the first stage of the process, the alkali metal hydroxide, the PEG and the oxygen donor form the reagent APEG. The reagent is then heated at 80°C-120°C and atmospheric pressure; a slight excess of reagent is necessary for the Cl neutralization.

#### 5.1.3. HYDROHALOGENATION

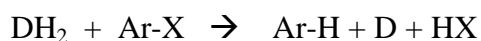
Under the category of hydrodehalogenation may be included all the reductive dehalogenation processes involving the breaking of a single bond between a carbon

atom and the halogen with the subsequent formation of a single bond between hydrogen and carbon. The process may involve the use of molecular hydrogen, similar to the hydrogenation of crude oil, or may be based on processes of catalyzed transfer of hydrogen from an hydrogen donor.

These process use palladium as a catalyst at atmospheric pressure. The catalyst, made by PdCl<sub>2</sub>, is anchored to a N-vinyl-2-pirrolidone support; the reaction operates at atmospheric pressure and 65°C, and is strongly poisoned by the HCl formation. Due to this, it is necessary to add a stoichiometric amount of a base in order to neutralise the acid.

The reduction reaction based on the use of Nickel-Raney as catalyst, are usually slower than the palladium based ones, requiring longer reaction times and higher temperatures. The advantage lies in the lower cost of the Nickel-Raney reagent, which however may be not enough to compensate for the inefficiency of the process.

The hydrogen transfer reaction is as following:



DH<sub>2</sub> = hydrogen donor

Ar-X = halogenated aromatics

D = (hydrogen acceptors)

Hydrogen donors may be hydrazine, ipophosphites, formiates, boron, aluminium, tin, silica hydrides, alcohols, amines, hydrocarbons, used homogeneous catalyst made of complex salts of palladium, platinum, ruthenium, iridium, iron, nickel, cobalt, or heterogeneous catalysts made mostly of palladium.

#### 5.1.4. GAS PHASE CHEMICAL REDUCTION (GPCR)

A gas reduction process uses high temperature hydrogen as a reducing agent to destroy chlorinated organic compounds. A process developed originally in Canada is the Gas-Phase Chemical reduction (GPCR). The process is based on gas-phase thermo-chemical reaction of hydrogen with organic compounds. At 850°C or higher, hydrogen combines with organic compounds in a reaction known as reduction to form smaller, lighter hydrocarbons, primarily methane. For chlorinated organic compounds, such as PCBs, the reduction products include methane and hydrogen chloride. This reaction is enhanced by the presence of water, which acts as a reducing agent and a hydrogen source.

The mixture of gases and vaporised liquids are heated as they pass electric heating elements situated around the central ceramic-coated steel tube of the reactor. Gases and any entrained fine particulates proceed up the central tube providing in excess of 2 seconds retention time at 900°C.

The reaction comes to completion before the gases reach the scrubber where the water, heat, acid and carbon dioxide are removed. A caustic scrubbing agent is added, if required, to maintain the scrubber water pH between 6 and 9. The temperature of the exit gas is maintained near 35°C by cooling the scrubber water using dual plate heat exchangers and cold water from an evaporative cooler.

Typical applications for GPCR include treatment of PCBs, electrical equipment, contaminated soils, petrochemical wastes, high-strength industrial chemicals, chlorofluorocarbons, carbon filter media, certain low level radioactive wastes, and municipal sludges.

#### Benefits

- low emissions
- treats all chlorinated molecules
- complete destruction
- converts chlorinated compounds into fuel

#### Disadvantages

- large fixed plant (Mobile and portable units available)
- use of hydrogen

#### 5.1.5. BCD DEHALOGENATION PROCESS

The Base Catalysed Dechlorination (BCD) process was developed from work by the USEPA RREL on earlier forms of dechlorination (in particular the "KPEG" process).

The BCD process can involve direct dehalogenation or decomposition of the waste material, or can be linked with a pretreatment step such as thermal desorption which yields a relatively small quantity of a condensed volatile phase for separate treatment by the BCD process.

The BCD process involves the addition of an alkali or alkaline earth metal carbonate, bicarbonate or hydroxide to the medium contaminated by PCB. The alkaline chemical may be added to the contaminated medium in an aqueous solution, or in a high boiling point solvent. If the chemical is added in the form of a solid dispersion or suspension

in water, the water assists in distributing the metal compound homogeneously throughout the contaminated medium. If the chemical is added with a high boiling point solvent, the solvent must have a boiling point of at least 200°C, and preferably be in the range from 200°C to about 500°C. Otherwise, it will distil from the mixture during treatment.

## 5.2. THERMAL DESTRUCTION OF PCBs

### 5.2.1. INCINERATION

Incineration is the chemical reaction of oxygen (oxidation) with a combustible material. A great advantage of the incineration process is that they are highly non specific: all organic compound present in the combustion stream are mineralized if proper incineration conditions are ensured.

The main process stages are:

- 1) drying and degassing – here, volatile content is evolved (e.g. hydrocarbons and water) at temperatures generally between 100 and 300 °C. The drying and degassing process do not require any oxidising agent and are only dependent on the supplied heat
- 2) pyrolysis and gasification - pyrolysis is the further decomposition of organic substances in the absence of an oxidising agent at approx. 400 – 700 °C. Gasification of the carbonaceous residues is the reaction of the residues with water vapour and CO<sub>2</sub> at temperatures, typically between 700 and 1000 ° C, but can occur at temperatures up to 1600 °C. Thus, solid organic matter is transferred to the gaseous phase. In addition to the temperature, water, steam and oxygen support this reaction
- 3) oxidation - the combustible gases created in the previous stages are oxidised, depending on the selected incineration method, at flue-gas temperatures generally between 800 and 1450 °C.

Different incinerator plant configurations may be considered for the purpose of PCB destruction:

**Rotary kiln.** Rotary kiln are the most widely used incineration plants. They are able to process a wide variety of wastes, and operate with different feeding rate. The waste is conveyed through the kiln by gravity as it rotates. Direct injection is used particularly for liquid, gaseous or pasty (pumpable) wastes – especially where they

have safety risks and require particular care to minimise operator exposure. Solid materials are usually fed through a non-rotating hopper. The residence time of the solid material in the kiln is determined by the horizontal angle of the vessel and the rotation speed.

Rotary kiln incinerators may operate at high temperature and usually allow a good mixing between solids and combustible and a continuous ash removal. The residence time of solids is easy to be managed, and the need for waste pre-treatment is very low. Disadvantages consist of the fact that rotary kiln incinerators may need system for controlling fugitive emission, are more subjected to thermal discontinuities due to the high heterogeneity of wastes processed, and have greater emission of particulates and HCl.

A small/medium size rotary kiln incinerator (up to 15t/day) should include the following components:

- Storage facility: The storage facility is a bunker maintained under negative pressure with a minimum overall area of around 2000m<sup>2</sup>. It is divided in 3 storage areas: storage and pre-treatment (shredding, oil removal) of PCB capacitors; storage and pre-treatment of PCB contaminated soil and concrete (crushing, sieving); storage and pretreatment (washing) of PCB transformers. An insulated conveyor belt carries waste from the storage facility to the incinerator. The storage facility should include a up to date waste characterization lab, by a computerized system for waste acceptance and labeling, and an air cleaning system (activated carbon and fabric filter).
- Rotary kiln: The rotary kiln should ensure a maximum operating temperature of at least 1000 °C. The kiln may have a length in the order of 10-13m, and an inner diameter of 1.7 -2.5 m, with a length/diameter ratio of 6-8. The rotation and inclination must ensure an estimated waste retention time from 0.5 to 1.5 hrs. The internal wall of the kiln is usually lined with a layer of refractory material with high content of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>
- Secondary Combustion Chamber (SCC): The vertical furnace is usually a stainless steel cylindrical structure, connected with the rotary kiln, equipped with two two-stage light diesel burners and a maximum operating temperature of at least 1200 °C.
- Pre cooling: The pre-cooling system is used in some plants with the purpose to



decrease temperature after the post-combustion chamber down to 950°C – 1000°C to prevent damage to the Venturi quencher. This system is basically a pre-quenching operating with two high pressure nozzles injecting a water/air mixture.

- Ventury quencher: In this device, the temperature of the stack gas containing HCl decrease suddenly from 950°C down to 80-95°C in less than 1s. The cooling and absorption medium is water.
- NaOH adsorbtion chamber: The NaOH absorption tower are based on counter or co-current spraying of a NaOH solution, for the neutralization of Chlorine.
- Fabric filter with lime and activated carbon injection: The fabric filter for the removal of fly ash should be equipped with injectors of lime and activated carbon. That would ensure further removal of PCDD/F and chlorine. The flow rate of the injectors can be adjusted continuously. Fabric filter must be equipped with a closed system for the removal of fly ash, which – due to high concentration of UP-POPs and heavy metals - is usually the most dangerous residue deriving from the incineration process.
- Activated carbon fixed bed: The activated carbon column (ACC) is the last barrier against the release of PCDD/F and PCBs in the atmosphere. ACC may allow for a further reduction of 2-3 times of the concentration of PCDD/F and PCBs remaining in the flue gas after fabric filters. Working temperature within ACC should not exceed 80-115°C, and the size of the ACC should be enough to ensure a proper reaction surface. Activated carbon must be incinerated once exhausted.
- Stack: The height and cross section of the stack must be properly designed, with the support of dispersion modeling analysis, to ensure good dispersion of the flue gas. The stack must be far from any aerodynamic obstacle that could prevent the proper dispersion of flue gases.
- Water treatment: The process wastewater treatment system may include adjusting pond, heat exchanger and cooling tower, desalination equipment for electro dialysis, reverse osmosis and evaporation, flocculation and precipitation tank, precipitate dehydrator, etc.. After treatment, the water may be recycled for use, so that the discharge of wastewater from the whole treatment process could be avoided.

### Liquid injection incinerator

Liquid injection incinerator relies on high pressure to prepare liquid wastes for incineration by breaking them up into tiny droplets to allow easier combustion. This configuration present several advantages:

- absence of mechanical components in the combustion chamber;
- limited generation of pollutants
- low maintenance and operational costs
- stability of the combustion process

These advantages are counterbalanced by several limitations:

- extensive pretreatment of wastes is required;
- suitable only for injectable wastes (liquids or fine dusts);
- risk of injector clogging in presence of incompatible wastes
- frequent maintenance / replacement of injectors may be required in presence of corrosive wastes

### Kilns and post combustion chambers for hazardous waste incineration

In the European BREF the following information are reported for the operational parameters of kiln and post-combustion chamber for hazardous wastes incineration:

- Operational kiln temperature: from 850 °C up to 1300 °C.
- Temperatures in the post combustion chamber (PCC) from 900 to 1300 °C

Most installations have the ability to inject secondary air into the post combustion chamber. Due to the high temperatures and the secondary air introduction, the combustion of the exhaust gases is completed and organic compounds (e.g. PAHs, PCBs and dioxins) including low molecular weight hydrocarbons, are destroyed.

### 5.2.2. PLASMA

Thermal plasma is a high temperature, partially or completely ionized gas. A thermal plasma is usually generated by an electric current (alternate at high frequency or continue) passing through the gas; the resistivity energy is dissipated by the gas which, with the increase in temperature, became conductive and able to sustain the electricity flow.

Plasma arc technology can create plasma using almost any type of gas (oxygen, nitrogen, carbon monoxide, air, etc.) and in a wide range of pressures (vacuum to 20 atmospheres). The plasma arc has a wide spectrum of temperatures ranging from 1500°C to over 7000°C.

The thermal plasma offer several advantages for the elimination of toxic wastes:

- The use of the electricity for the production of heat eliminates or greatly reduce the use of air for the combustion process; if an inert gas is used for generating the plasma, this render it actually a pirolysis process leading to the destruction of waste without oxidation.
- The high energy density and the high temperature allow for a great throughput in small size reactors.
- The switch on / switch off time for a plasma plant is usually very short, making it possible to use these it in a discontinuous way,

On the other side, the biggest shortcoming of plasma lies in the fact that electricity is not the most efficient way to produce thermal energy, thus plasma process are rather inefficient from the thermodynamic point of view. This shortcoming however become negligible for the treatment of waste that are inert and decompose only at very high temperature, or which for other reasons cannot be burnt directly by incinerators.

**Plant components :** Depending on the waste to be treated, a typical plasma plant would be composed by the following components:

- 1) Electric system: as the plasma relies on electricity as sole energy source, a suitable electricity source is the key for the proper working of the unit. Plasma usually operate at high voltage and current. A medium size plasma plant operates at a current in the order of 1000A and at a voltage of around 500V. Small plasma units, like the Plascon plasma suitable only for liquid waste, have an electricity consumption is in the order of 180KW, which can be supplied by a 300KW generator. The electrical system would then include a transformer substation to bring electricity to the desired voltage, safety switchgears, high voltage connections, control panels.
- 2) System for the generation / supply of inert gases: Plasma torches are typically supplied with a small inert gas flow rate which flows through – and actually supports – the electric arc. The gas is usually diatomic (such as Nitrogen) or

monoatomic (such as Argon or Helium). The inert gas supply system is usually made of an inert gas storage and an injection system. In rare cases, the inert gas may be generated on site.

- 3) System for the generation / supply of oxygen: Oxygen is used in some plasma process as a reagent with exhaust gas generated by the thermal destruction process. In some plants, exhaust gas made of carbon and hydrogen is made reacting with a stoichiometric amount of oxygen to generate a CO and . CO and H<sub>2</sub> are subsequently recovered or burnt in a flare, to generate CO<sub>2</sub> and H<sub>2</sub>O.
- 4) Waste feeding system: Depending on the type of waste, waste feeding may take the form of an injection system of liquid waste, or of a batch feeding for solid or semisolid waste. The waste feeding system may include waste storage, pretreatment and mixing.
- 5) Plasma torch and plasma reactor: Plasma torches and plasma reactor are the core part of the system. There are basically two different types of plasma torches and plasma reactors:
  - a) Non-transferred arch: In a non transferred arc plasma torch, the material of the electrodes does not take part in the plasma generation. The reagents for the plasma generation may be provided directly by the waste to be treated. However, in this case the interaction of corrosive component, like chloride, with the electrodes may cause their erosion. For this reason, in the non transferred arc torches, reagents for the plasma generation are usually injected downstream to the electrodes. The plasma arc torch uses copper electrodes to create a non-transferred arc. The plasma torch and electrodes are water-cooled and the average life of the electrodes ranges between 200 to 500 hours of operation. A DC power supply unit provides the electrical requirements of the torch and commercial units are available in power levels ranging from about 100 kW to 10 MW capacity.
  - b) Transferred arch: In the transferred arch, one of the electrodes is the substance to be treated. Wastes may be introduced in the reactor as liquid or solid: the exposure to the heat generated by the arc cause the pyrolysis of the organic component of the waste and the vitrification of the inorganic components. Electric Arc furnaces in the metallurgic industry may be considered as a special kind of plasma transferred arch.

- 6) Cooling system: Cooling of electrodes is usually obtained by means of a water cooling circuit, refrigerated by evaporative or air cooling units. Usage of water for cooling the electrodes may range from less than 2 m<sup>3</sup>/hr to tenths of m<sup>3</sup>/hr, depending on the amount of water recirculated in the system, and on the system size and design
- 7) Flue gas treatment system: The flue gas treatment system may be very specific for the type of waste disposed by the plasma plant. More specifically, for plants used for destroying chlorinated compounds, the following components are required:
  - a) a rapid quencher, for ensuring the instantaneous cooling of the exhaust gas and preventing the “de-novo” formation of dioxin;
  - b) a system for the recovery of chlorine. This is usually made by spraying the gas with an alkaline solution in the quencher.
  - c) Other flue gas treatment components that may be present in a plasma plant are: Post-combustor, syngas recovery system, cyclone separator, quencher, AC filters, HEPA filters, scrubbers, flares, etc.
- 8) Water treatment system: Although a water treatment system is not always necessary for treatment of the plasma wastewater effluent, depending on the features of the waste feeded, the water coming out from the quencher and the neutralizer may contain concentration of salts that may be recovered for the purpose of recirculating the water, or to have the water compliant with the regulatory limits. Water treatment system may be composed by evaporator modules or by reverse osmosis units for the removal of salts, and by filters for the removal of particulate.
- 9) Waste collection system: there is no need of a system dedicated to the collection or storage of solid waste for plasma units treating only liquid waste, with the exception of small amount of sludge or high concentrated saline solution from the wastewater treatment system. Plasma dedicated to the disposal of solid waste would generate as a solid waste inert, vitrified solid waste which are not dangerous and which can be usually be disposed in a landfill for non hazardous waste.
- 10) Online monitoring: The online monitoring system for plasma would mainly include:
  - a) an online monitoring system for measuring the concentration of NO<sub>x</sub>, SO<sub>x</sub>, O<sub>2</sub>, dust, HCl;

- b) an online system for the monitoring of the main operational parameters, like the plasma voltage and current, reactor temperature, pressure, etc.

## **6. DECONTAMINATION TECHNOLOGIES FOR EQUIPMENT AND WASTE**

### **6.1. RETROFILLING**

Retrofilling is a common technology used for reducing the contamination of PCBs in the dielectric oil of transformers under a prefixed concentration.

Retrofilling basically consists in replacing the PCB contaminated dielectric oil contained in transformers with clean dielectric oil. After the first retrofilling cycle, the PCBs contained in the porous media (wood and insulating paper) will be gradually released in the non contaminated oil, so that at the equilibrium the PCBs concentration in the dielectric oil of the transformer will be:

$$C_e = \frac{C_o V_p + C_1 V_s}{V_p + V_s}$$

Where  $C_e$  is the equilibrium concentration of PCBs in the dielectric oil,  $C_o$  is the initial concentration of PCBs in the dielectric oil,  $V_p$  is the interstitial volume of the porous material,  $C_1$  is the concentration of PCBs in the clean oil, and  $V_s$  is the internal volume of the transformer. To reach equilibrium concentration could require, in normal condition, a significant amount of time, therefore – due to the fact that a transformer under treatment represents an immobilized capital cost – several methods have been adopted to reduce treatment time, including applying heat and vacuum to the transformer under treatment, recirculating several times the cleaned oil etc. When feasible, the most economic way of performing retrofilling is however to perform an accurate draining of the oil, and then to place again the transformer in use; after some months, the PCBs concentration in the transformer is checked, and if necessary the retrofilling process is repeated.

### **6.2. SOLVENT WASHING**

Solvent extraction is a technology based on the partition of chemical species between two immiscible phases. . The concentration ratio reached at the equilibrium between the two phases is specific for the compound and for the two solvent. For instance, the

Kow partition coefficient is the ratio at the equilibrium between the concentrations of the compound in octanol and water:  $Kow = \log (C_{oct}/C_w)$ . PCB are compound characterised by a high Kow value and by a low solubility in water, which means that these compound are very lipophilic and hence, can be hardly extracted from contaminated media like oils or soils with high O.C. content. In order to chemically extract PCB from contaminated oils it is then necessary to use a great amount of the proper solvent for the extraction process, and also to have a system for the pretreatment of the media and for the concentration / separation of PCBs from the solvent. Thus, despite the process is conceptually simple, its application may be quite complex, and different firms developed patented solution concerning both solvent formulations and separation / distillation systems. The PCBs molecules are not destroyed but only removed from the contaminated media, thus this technology may be only used as part of a train of decontamination processes.

Solvent extraction processes can be divided into three general types based upon the type of solvent used: standard solvents, near-critical fluids/liquefied gases, and critical solution temperature (CST) solvents.

Standard solvent processes use alkanes, alcohols, ketones, or similar liquid solvents typically used at ambient pressure. The system may be operated in either a batch or continuous mode and consists of four steps: (1) extraction, (2) separation, (3) desorption, and (4) solvent recovery.

## **7. SOLVENT EXTRACTION**

### **7.1. THERMAL DESORPTION AND VACCUM ENHANCED THERMAL DESORPTION**

Thermal desorption may be defined as “a process that uses either indirect or direct heat exchange to heat organic contaminants to a temperature high enough to volatilize and separate them from a contaminated solid medium”. Air, combustion gas, or an inert gas is used as carrier for the vaporized components. Thermal desorption systems are therefore physical separation processes that transfer contaminants from one phase to another. They are not designed to provide high levels of organic destruction, although the higher temperatures of some systems will result in localized oxidation or pyrolysis. Thermal desorption is not incineration, since the destruction of organic contaminants is not the desired result. The bed temperatures achieved and residence times used by thermal desorption systems will volatilize selected contaminants, but

usually not oxidize or destroy them. System performance is usually measured by the comparison of untreated solid contaminant levels with those of the processed solids. The contaminated medium is typically heated to 300 to 1,000 °F, based on the thermal desorption system selected.”

Low-temperature thermal desorption (LTTD) is a physical separation process that treats wastes at 90 to 320°C (200 to 600°F) to volatilize water and organic contaminants. A carrier gas or vacuum system transports volatilized water and organic contaminants to the gas treatment system. The bed temperatures and residence times designed into these systems will volatilize selected contaminants but typically will not oxidize or destroy them. LTTD is a full-scale technology that has been proven successful for remediating petroleum hydrocarbon contamination in all types of soil. Decontaminated soil retains its physical properties and ability to support biological activity.

In the High Temperature Thermal Desorption (HTTD), wastes are heated to 320 to 560°C (600 to 1,000 °F). HTTD is frequently used in combination with incineration, solidification/stabilization, or dechlorination, depending upon site-specific conditions. The technology has proven to produce a final contaminant concentration level below 1 mg/kg for the target contaminants identified.

Two common thermal desorption designs are the rotary dryer and thermal screw. Rotary dryers are horizontal cylinders that can be indirect- or direct- fired. The dryer is normally inclined and rotated. For the thermal screw units, screw conveyors or hollow augers are used to transport the medium through an enclosed trough. Hot oil or steam circulates through the auger to indirectly heat the medium.. Most of these units are transportable.

Thermal desorption places constraints on the physical form of the waste to be treated, depending on the type of thermal desorber being used.

In the case of indirectly heated rotary kilns, a range of waste types can be treated. However, a typical feed size limitation of 25 mm usually applies (Carlisle, 1994a; Tozer, 1994; Krynen, 1994a). If this size is exceeded, then the desorption can be incomplete or the desorber mechanism may be blocked (this is dependent on the desorber system). In practice, desorption can be enhanced by increasing the temperature or by adding reagents. Higher boiling point waste materials such as PCBs and chlordane may not desorb effectively unless a reagent such as sodium bicarbonate is added to the mixture.



If thermal desorption is conducted with indirect heating under high vacuum in a closed system, the following advantages can be obtained:

- Reduction of the process temperature;
- Reduction of the exhaust gases volume
- Reduction of energy requirements.

However, the need to operate in a closed system implies operation in batch, which would somehow limit the throughput.

## **8. INTEGRATION OF TECHNOLOGIES**

Retrofilling, solvent washing and thermal desorption cannot be considered as the disposal technologies because it involves only the physical transfer of the POPs without destroying it. Therefore integration of technologies is important.

Retrofilling is suitable for low concentration of PCB in large PCB transformer. So the destruction technologies of the PCB are integrated which are followed by incineration of dielectric oil and dehalogenation followed by regeneration of oil. These integration technologies involve cost constraints like cost for dehalogenation, mainly the cost of metallic sodium, cost of incineration and the cost of dielectric oil.

## **9. DESIGN CONSIDERATION FOR THE SELECTION OF SITE FOR THE DISPOSAL OF PCB DISPOSAL**

The selection of the site for the disposal of PCB depends on the logistics, infrastructure, environmental and permitting aspects.

Logistic aspects: For the selection of site, the distance of site from PCB equipment is important, including the storage area for PCBs. Transportation cost also includes the cost for the handling and disposal of PCB. The disposal facility of PCB includes transportation plan, transportation infrastructure and disposal facility.

Infrastructure aspects: For the establishment of PCB plant, the availability of the utilities such as portable water, electricity and steam are necessary. For the establishment of chemical dehalogenation plant, steam is necessary and for incineration availability of water is needed for cooling.

Environmental aspects: Environmental aspects like effect of PCB plant on the environment and on the meteorological risks or natural events like floods, risk etc are

to be considered. So the environmental impact assessment is mandatory for the selection of site.

Permitting aspects: Rules governing the minimum distance of the water bodies and population is necessary for the selection of the site for the disposal of PCB. Public awareness on the disposal of PCB is mandatory.

## **10. CONDUCTION OF NO LOAD AND PROOF OF PERFORMANCE TESTS**

Before starting the operations, any technology needs to be accurately verified by means of no load tests and proof of performance test. Both no load and proof of performance tests are usually strictly related to the technical specification set by the bidding documents; Therefore it is extremely important, while drafting technical specification, to set forth these test requirements and standard which are SMART, i.e. Specific, Measurable, Attainable and Relevant and Time bound.

Therefore, while defining criteria for requirements or standards though important, cannot be directly measured, it is always recommended to find out indicators that may be considered representative of the desired standard. For instance, an availability of 20 hours per day over one or two week, followed by a thorough assessment of the plant conditions after the test run, may be considered as a good indicator of an availability of 18/24 over 230 days/year.

### **10.1. NO LOAD TESTS**

No load test have the main purpose to check the functionality of the disposal facility from the point of view of proper working of each facility component, presence of air or liquid leakage points, correctness of the electrical layout, effectiveness of the control and monitoring system, verification of the technical and operational parameters. For technologies working at high temperatures, like incinerators or thermal desorber, necessary activities for the preparation of refractory material to withstand high temperature by means of progressive heating under programmed temperature ramps must be completed before the no-load runs are carried out.

No load test must be carried out firstly on each separate component of the plant, and secondly on the whole system. No load test runs should be carried out with POPs free waste stream, in all the case where running the equipment in absence of any waste load can be either not representative or even dangerous for the equipment.

No load test should then include:

- The test of the remote control software and of the servomechanisms and sensors governed by the software, including the verification of the logic of the plant and of the control system;
- The complete test of the electric system (motors, switches, activators) and of its safety devices
- The complete test of the hydraulic and the pneumatic systems
- Complete test of the fuel systems and burners
- Tests of the online monitoring system,
- Test of chemical feeding system;
- Tightness of reactors, tanks, pipes;
- Separate test for any subcomponent, like water treatment system, air pollution control system, waste pretreatment and feeding system, etc.

A complete no-load test plan with procedures and acceptance standards must be included in the operational manual of the disposal facility.

## 10.2. PROOF OF PERFORMANCE TESTS

Proof of Performance testing is intended to ensure that the technology operates in accordance with the technical specifications, is adequate to perform as warranted by the bidder, and substantiates a satisfactory level of performance reliability prior to its acceptance. The detailed Proof of Performance test protocols and acceptable parameters should be approved by the contracting parties before the testing is carried out. In general, proof of performance test should cover a set of conditions selected as the most common operational conditions, together with some “extreme” conditions which may occur during the operational life of the plants.

The purpose of the proof of performance test is twofold:

- To identify the operational conditions under which the plant may operate safely and in compliance with the required technical and environmental standards;
- To verify that the plant can effectively comply with BAT/BEP requirements and standards, and with the legislative standards on emission of pollutants in the atmosphere and in the other process streams.

The Proof of Performance Test plan must be carefully agreed upon among the parties, and the following details should be defined:

- Clear conditions for sharing operational costs during test;
- DE and DRE values to be attained;
- Operational, environmental and emission standards to be complied with;
- Duration of the proof of performance test;
- Amount of different waste categories to be treated during the proof of performance test, and the concentration of PCBs and other POPs in each waste;
- Methodologies for preparing waste to be treated and for measuring PCB concentration in the input waste stream;
- Number of runs to be performed for each waste category;
- Number of samples to be taken for each run;
- Location of sampling points;
- Clear conditions for the acceptance of the test results, including the arrangements for the third party verification for the compliance of the Proof of Performance Test results with the standards.
- Conditions which apply in case one or more runs or sampling result do not comply with the standard;
- Conditions which apply in case of test failure;
- Sampling methodology and standards;
- Analytical methodology and standards;
- Emergency measures
- Training on PPE and Hazop