2015

Guidelines For PCBs, PCB-Containing Equipment and Waste Disposal

Table of contents

1. FOREWORDS

The main purpose of this document is to provide practical indications for selecting and assessing the disposal technologies for PCBs. This activity is part of the UNIDO/GEF project "Environmentally Sound Management and Final Disposal of PCBs in India"

Only commercially available technologies for the disposal of PCBs are included in this document, and their process principle and chemical mechanism are summarized. Due to the great variability in the costs reported for establishing the same technology in different countries, cost figures for these technologies have not been reported here. However, the main advantages and shortcoming of each technology are discussed.

The International and National legislative framework regulating the establishment of disposal technologies in India are discussed, together with recommendations in setting standards and conducting No-load and Proof of Performance tests.

2. INTERNATIONAL STANDARDS ON THE DISPOSAL OF POPS

2.1. STOCKHOLM CONVENTION

Under the Stockholm Convention on Persistent Organic Pollutants (POPs),

Article 5 (Measures to reduce or eliminate releases from unintentional production) states:

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 article provides the definition of BAT, BEP, techniques and sources as follows:

(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."*

Article 6 (Measures to reduce or eliminate releases from stockpiles and wastes) states: Take appropriate measures, such that, the 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.

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".*

Of particular relevance are:

- Annex C, Part II Source Categories (a): waste incinerators
- Annex C, Part II Source categories (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 the assessment of technologies, due to their specific and intrinsic features, to ensure that the emission of UP-POPs is kept to a minimum or even completely avoided. This concept is well described in the following sentence extracted from Section II of the BAT/BEP guidelines:

Decision makers are encouraged to use a checklist approach when they give consideration to alternatives in the application of best available techniques to a proposal to construct a new facility or significantly modify an existing facility that uses process that releases chemicals listed in Annex C.

In doing this, they should keep in mind the overall sustainable development context, and they should take 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 the document, 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[1] remarks: *more restrictive technical and environmental performance standards would not be applied to GEF financing of POPs disposal in developing countries and Countries with Economy in Transition than are applied in developed countries.*

In the selection of alternatives it is crucial to note 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. THE BASEL CONVENTION

Under the Basel Convention, guidelines are periodically amended and constitute as the basic guidance document with minimum standards applied to the POPs stockpiles and waste disposal technology used in GEF funded projects. Of particular relevance to the disposal of PCBs are the following guidelines:

- 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 European Commission, after a 2 year review process, adopted a proposal for an Industrial Emissions Directive (Integrated Prevention and Pollution Control). The proposed directive was a recast of 7 existing pieces of legislation and its aim is to achieve significant benefits to the environment and human health by reducing

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[1] Selection of Persistent Organic Pollutant Disposal Technology for the Global Environment Facility A STAP advisory document, November 2011

harmful industrial emissions across the EU, in particular, through better application of BAT.

The technical pillar of the EU IPPC is the guidance provided by BREFs documents (BAT Reference documents). These documents analyze the technologies which have to be considered at EU level as reference BAT, and cover several sectors, of which the ones which are most interesting from the point of view of PCBs disposal are:

- Common Waste Water and Waste Gas Treatment/ Management Systems in the Chemical Sector;
- Waste Incineration;
- Waste Treatment Industries

These documents have been drafted keeping the European Member States as target. But the information they contain is mainly technical and is used as BAT technical reference in many countries, even though some of the BAT technologies or some of the capability needed to operate these technologies may not be readily available in all the countries. Extensive reference has been made to the European BREF documents in drafting the Stockholm Convention Guidelines on Waste Incineration and Waste Treatment.

2.4.   INDIAN EMISSION STANDARDS

The Central Pollution Control Board (CPCB) has developed National Standards for Effluents and Emission under the statutory powers of the Water (Prevention and Control of Pollution) Act, 1974 and the Air (Prevention and Control of Pollution) Act, 1981. These standards have been approved and notified by the Government of India, Ministry of Environment and Forests, under Section 25 of the Environmental (Protection) Act, 1986. Till now, Effluent standards for 37 categories of Industries and Emission standards for 31 categories of Industries have been evolved and notified besides standards for ambient air quality, ambient noise, automobile and fuels quality specifications for petrol and diesel. Common Hazardous Waste Incinerators are required to comply with the gaseous emission norms notified under the Environment (Protection) Fifth Amendment Rules, 2008, dated 26 June 2008.

Table 1: Gaseous Emission Norms for Common Hazardous Waste Incinerators

		Limiting Concentration in mg/Nm^3, unless stated	Sampling Duration, in minutes, unless stated
Common Hazardous Waste Incinerator	Particulate Matter	50	30
	HCl	50	30
	SO$_2$	200	30
	CO	100	30
		50	24 hours
	Total Organic Carbon	20	30
	HF	4	30
	NO$_x$ (NO and NO$_2$ expressed as NO$_2$)	400	30
	Total dioxins and furans	0.1 ngTEQ/Nm^3	8 hours
	Cd + Th + their compounds	0.05	2 hours
	Hg and its compounds	0.05	2 hours
	Sb + As + Pb + Co + Cr + Cu + Mn + Ni + V + their compounds	0.50	2 hours

	NOTES:
	i. All monitored values shall be corrected to 11% oxygen on dry basis.
	ii. The CO_2 concentration in tail gas shall not be less than 7%.
	iii. In case, halogenated organic waste is less than 1% by weight in input waste, all the facilities in twin chamber incinerators shall be designed to achieve a minimum temperature of 950 °C in secondary combustion chamber and with a gas residence time in secondary combustion chamber not less than 2 seconds.
	iv. In case, halogenated organic waste is more than 1% by weight in input waste, waste shall be incinerated only in twin chamber incinerators and all the facilities shall be designed to achieve a minimum temperature of 1100 °C in secondary combustion chamber with a gas residence time in secondary combustion chamber not less than 2 seconds.
	v. Incineration plant shall be operated (combustion chambers) with such temperatures, retention time and turbulence, as to achieve Total Organic Carbon (TOC) content in the slag and bottom ashes less than 3%, or their loss on ignition is less than 5% of the dry weight.

3. INDIAN LEGISLATION ON THE DISPOSAL OF HAZARDOUS WASTE AND PCBS

3.1. PERMITTING AND ENVIRONMENTAL IMPACT ASSESSMENT

Under the Hazardous Waste Rules, 2008,

Chapter II (Procedure for Handling Hazardous Wastes), Article 5 states:

Every person who is engaged in generation, processing, treatment, package, storage, transportation, use, collection, destruction, conversion, offering for sale, transfer or

the like of the hazardous waste shall require to obtain an authorization from the State Pollution Control Board.

Although an Environmental Impact Assessment is not required for hazardous disposal facilities under the Indian Legislation on Environmental Impact Assessment, a disposal facility financially supported by the GEF, or operating in the framework of GEF supported projects, should be subjected to an internationally benchmarked environmental assessment (EA), and should have some form of Environmental Management Plan (EMP) in place. EMP should include:

- Regular monitoring and reporting on pollutant emission at the source;
- Regular environmental monitoring and reporting
- Periodical assessment of the Destruction Efficiency and Destruction and Removal Efficiency
- Safety at work and Personal Protective Equipment.

4. CRITERIA FOR EVALUATING PCBS DISPOSAL EFFICIENCY

4.1. DE AND DRE

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

DE takes into account the overall destruction efficiency, including residues of 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

DE calculated as TEQ

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

$$OUT = \int_{t=0}^{t=end} Q_s \left(CS_{PCB+TCDD\,/\,F\,(TEQ)}\right) + \int_{t=0}^{t=end} Q_{BA}\left(CBA_{PCB+TCDD\,/\,F\,(TEQ)}\right) + \int_{t=0}^{t=end} Q_{FA}\left(CFA_{PCB+TCDD\,/\,F\,(TEQ)}\right) +$$

$$+ \int_{t=0}^{t=end} Q_{SL}\left(CSL_{PCB+TCDD\,/\,F\,(TEQ)}\right) + M_{AC}\left(CAC_{PCB+TCDD\,/\,F\,(TEQ)}\right)$$

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:

Wpcb: 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%.

Destruction and Removal Efficiency (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 Efficiency (DE) and Destruction and Removal Efficiency (DRE) should be verified and reported for any substances of concern undergoing destruction, as demonstrated by multiple samples tested using internationally recognized analytical methods and measured at a frequency sufficient to ensure compliance with this criterion during disposal operation. (Note: "substances of concern" refer to chemicals that have the characteristics of environmental persistence, bio-accumulation, potential for long-range environmental transport, and potential for damage to human health and the environment, as described in Annex D of the Stockholm Convention) Destruction Efficiency (DE) and Destruction and Removal Efficiency (DRE) should be not less than 99.9999%.

Compliance with DE means that the technology not only effectively eliminates gaseous air-emissions of substances of concerns (with special reference to PCDD/F) but it also effectively eliminates releases of these pollutants in the solid wastes and liquid wastes.

4.2.   INFLUENCE OF PRE-TREATMENT ON DE AND DRE

The PCBs (measured or estimated) released during storage or pretreatment should be included in the calculation of DE and DRE.

For example, in the case of a disposal process based on the following steps:

- equipment opening and un-assembling;
- solvent extraction;
- recovery of decontaminated metal scraps;
- incineration of pure PCBs;
- Chemical Dehalogenation of the oil and of the recovered solvents

It may be envisaged that the bulk of PCBs release could occur in the first stage, resulting from direct release of PCBs in to the environment or residues remaining in the porous component of the equipment.

The final disposal efficiency (DE) of the whole process is, therefore, governed by the amount of PCBs still present in the treated material or released during the opening of the PCBs equipment, which would comparably be much greater than the release with the exhaust gases or the untreated PCBs after dehalogenation.

Although the evaluation of DRE usually only quantifies the concentration of POPs 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 of DRE when properly evaluated.

In the case of incineration, these are for instance:

- Fugitive emissions from the kiln inlet during loading, due to fault or poor performance of the negative pressure system;
- Emission of POPs contaminated dust / vapors from the storage area (either as fugitive emissions or as conveyed emission if the storage facility is equipped with an air pollution control system);

Practically, this means that proper countermeasures 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.

Moreover, when analyzing the efficiency of a plant, all the possible sources of emission (not only the emission from stack) should be identified and considered.

Figure 1 – Relevance of pre-treatment on DE values.
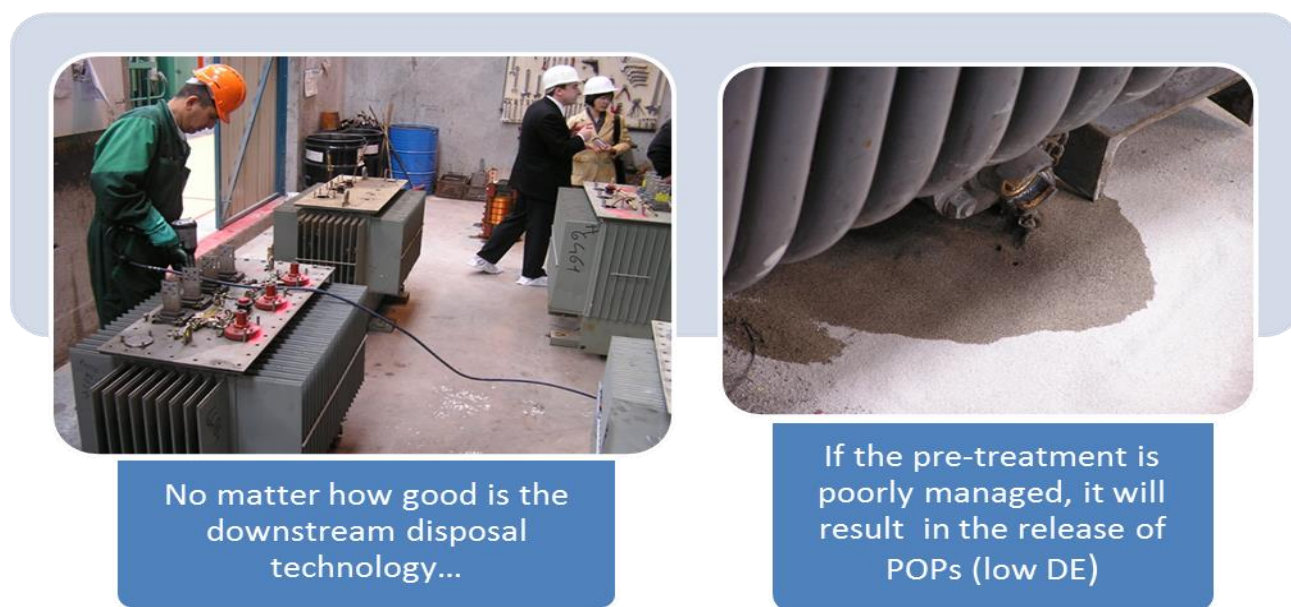
4.3.   SHORTCOMINGS OF THE DE AND DRE APPROACH

The following shortcomings of the DE and DRE approach should be taken into due consideration:

1. DRE does not take into account POPs residues remaining in process streams like ashes, sludge, and waste generated during pre-treatment. For this reason, DRE should be always integrated by the measurement of DE and proper monitoring of POPs in all the outflow streams.

2. The concentration or POPs (including PCDD/F and PCBs) in the output stream is not linearly related to the concentration of POPs in the input stream. In case of incineration, PCDD/F emission at the stack would not fall below certain values even in case of low chlorine concentration of the waste fed to the plant, due to the fact that PCDD/F may also be generated during the combustion of clean fuel. For desorption technologies, there is a lower limit for the removal of PCBs or other POPs from the waste which is more related to the intrinsic characteristics of the technology rather than the concentration in the input stream. Therefore, the treatment of waste with low concentration of POPs would result in higher DE and DRE values, even if the concentration in the process stream is well within the emission limits accepted for BAT and BEP.

3. The value of DE and DRE depends upon the detective limit and the analytical sensitivity of the method adopted.

4. DE and DRE do not provide information of the transformation of PCBs to other POPs or substances of concern. Therefore, a thorough knowledge of the disposal process could ensure that the disposal technology does not generate any toxic by-products.

5. DE and DRE do not provide any information on the absolute value of the mass of pollutant released to the environment. These indicators should always be evaluated taking into consideration the flow rate of the exhaust gas and the mass flow rate of the other process stream.

6. DE and DRE are usually measured only during Proof of Performance Tests. These tests are carried out to ensure that the 1) test conditions are representative of the operational condition of the plant and 2) tests are carried out within a proper range of operational conditions.

The Environmental Management Plan should include the measurement of DE and DRE at regular intervals (for instance, once per year).

Figure 2 – An air pollution control system treating the emission generated by a PCB waste storage.

Figure 3 – The releases through the whole waste management cycle should be considered when calculating the DE.

Site cleanup

Transportation and Storage

Final Disposal
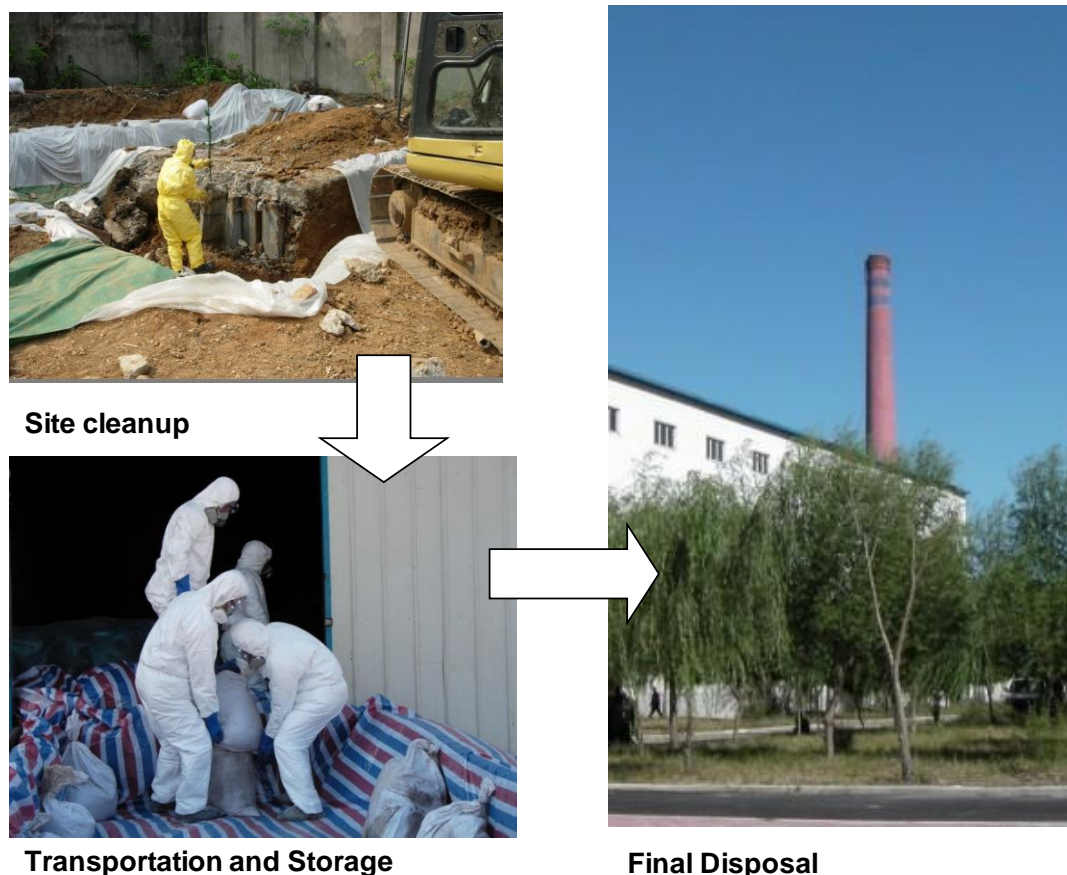
5. AVAILABLE TECHNOLOGIES FOR PCBS DISPOSAL

In the following sections, the main technologies used worldwide for the disposal or decontamination of PCBs containing equipment and oil are briefly described. The number of technologies listed is not exhaustive. Some technologies, which proved promising at laboratory or pilot scale, but are not yet fully available at commercial scale, are not included.

Indeed, it should be noted that only few technologies were until now demonstrated in the GEF projects for the disposal of PCBs. These are:

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

- Decontamination of the equipment by solvent washing

In addition to the above technologies, the following, which are commercially available in at least one country, have been included:

- Plasma
- Hydrodehalogenation

5.1. CHEMICAL DESTRUCTION OF PCBS

5.1.1. Metallic Sodium Dehalogenation Processes

Process Chemistry: In the mid-1850s, French chemist Adolphe Wurtz discovered that the reaction of an alkyl halide with metallic sodium removes the halide from the molecule to produce a sodium halide and a saturated aliphatic hydrocarbon. The general expression for the Wurtz reaction is:

$$2RX + 2Na \longrightarrow R\text{-}R + 2NaX$$
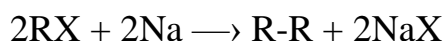
Where: R is the alkyl radical and X is the halogen atom.

The concept of the Wurtz reaction was expanded by Fittig in the mid-1860s. According to him, in the presence of metallic sodium, hydrocarbons containing a combination of an alkyl radical and an aromatic residue could be synthesized. The general representation of the Wurtz-Fittig reaction is:

$$ArX + RX + 2Na \longrightarrow Ar\text{-}R + 2NaX$$
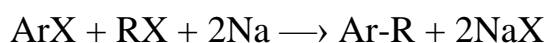
Hence, once the bond is broken and a new molecule is formed with sodium, the reaction is not reversible under the conditions that exist in the reactor. This eliminates the formation of toxic halogenated by-products from the treatment process. The destruction process is also applicable to many non-halogenated compounds containing reactive groups that are sensitive to attack by sodium.

Process Description: Sodium is a reactive metal which reacts violently with water to give hydrogen gas, creating a potential fire hazard. Hence, processes that use metallic sodium usually require 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-scale and full-scale conditions, the organic by-products are either combusted or

recovered, following refinement for appropriate post-treatment uses (e.g., energy recovery, reuse as dielectric fluids). The inorganic by-products (together with the excess sodium added initially to the system) is recovered and disposed of in an appropriate manner.

The introduction of metallic sodium into a PCB oil results in a reaction whose rate is dependent on the metal-oil interface. Finer the metal particles, the faster will be the reaction.

Secondary reactions occur during the dechlorination step, where 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.

The key research issues for the optimization of this technology deals with:

- Development of fine dispersed emulsions capable of increasing the oil/metallic sodium interface, at the same time being stable enough to minimize the risk related to the high reactivity of metallic sodium;
- Development of processes which can avoid the formation of polymers containing chlorine during the dehalogenation process;
- Development of processes which are non-destructive to the dielectric properties of the oil.

In general, sodium dispersions proposed today are extremely fine emulsions, having a high metal surface area. The dispersion is used at a temperature greater than the melting point of the sodium, i.e., 98°C (normally in the range 110°C – 180°C), and at atmospheric pressure. The metal surface can be renewed continuously to achieve a reasonable reaction rate and thus, decreasing the cost of the decontamination process.

Application: This technology may be adopted for the decontamination of the transformer oil in a closed loop decontamination process, or for the decontamination of PCBs contaminated oil. This technology is usually not suitable for the decontamination of contaminated soil and wastes. However, in some cases, this process has been used for the dehalogenation of the oily fraction of landfill leachate or to as fluorescent light ballast waste and capacitors.

Advantages:

1. The reaction is completed in a short time.

2. The oil decontaminated by metallic sodium dechlorination usually may be reused.

3. Metallic Sodium dechlorination is usually performed at low temperature (110° - 180°C) and at atmospheric pressure.

4. Strong enthalpies of formation preclude a reversal of the reaction once the original chemical has been degraded.

5. Capital investments are relatively low.

Limitations:

1. The rate of reaction (and, hence, the rate of exothermic heat generated by the reaction) must be controlled by the rate at which the waste is added to the sodium dispersion. The process requires the dewatering and degassing of the matrix to be treated.

2. The cost of metallic sodium prevents the use of this technology for the treatment of pure PCBs waste streams.

3. The strong oxidizing power of the metallic sodium could in some cases have a negative impact on the dielectric properties of the oil.

4. Build-up of biphenyls in oil may have a negative impact on its technical properties.

5. In addition, the dehalogenation of pure PCB results in a stream mainly composed by biphenyls and sludge made of polymerized polyphenyls and sodium chloride. The polyphenyls / sodium chloride sludge may be easily separated from the process stream: however to remove biphenyls from the oil used in the reaction batch, a specific distillation process would be required.

This problem is addressed by vendors with different approaches. One approach is based on a batch process using roughly 90% new insulating oil and 10% PCB. The new oil is reused in subsequent dehalogenation batches. The issue of biphenyls building up in the oil being re-circulated is disregarded, as the process is intended only for cleaning PCB transformers that would be subsequently dismantled. This approach is based on the assumption that the reuse of pure PCB transformers cannot be considered economically feasible, because once filled with non PCB oil these transformers have to be de-rated. Based on this assumption, this process is oriented

toward the dismantling of transformers. Transformers need to be manually dismantled and subsequently washed with a dedicate solvent washing process.

In other approaches envisaging the use of pure PCB transformers, the dilution of the oil to be processed is obtained by washing in a closed loop the carcasses of PCB pure transformers with cleaned oil. Due to the cost of new dielectric oil, this technology may be very expensive unless coupled with a second technology for refining the transformer oil.

Another key aspect is the relative efficiency of the Sodium dehalogenation reaction. Depending on the technology configuration, the amount of sodium required for destroying one ton of PCBs ranges from around 0.4 to 0.9 kg per kg of PCBs. In Table 2, comparison of the reaction efficiency among two metallic sodium technologies is reported.

Table 2: Reaction Efficiency of 2 MSD technologies

Supplier	Technology A	Technology B
Arochlor type	1242	1254
Amount PCB (tons)	1	1
Moles PCB	3882.92	3063.52
Moles Cl	11648.77	15317.60
Moles Na	11648.77	15317.60
Cl (tons)	0.41	0.54
Na (tons)	0.27	0.35
Na consumption declared	0.41	0.93
Reaction efficiency	65.09	37.90
NaCl produced	0.68	0.90
Biphenyls produced	0.60	0.47
Waste (sludge)	1.28	1.37

5.1.2. A-PEG Dehalogenation processes (Glycolate/Alkaline Polyethylene Glycol)

Process Description: Glycolate dehalogenation makes use of a chemical reagent called A-PEG. A-PEG 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 can also been used for this process.

The process consists of mixing and heating of the contaminated media with the A-PEG reagent. In the first stage of the process, the alkali metal hydroxide, the PEG and the oxygen donor form the reagent A-PEG. The reagent is then heated to 80°C-120°C at atmospheric pressure; a slight excess of reagent is necessary for neutralization of Cl.

During heating, the alkali metal hydroxide reacts with the halogen from the contaminant to form a non-toxic salt. The PEG takes the location in the PCB molecule formerly occupied by the halogen making it less hazardous. The reaction, a nucleophilic substitution, is due to the alkoxy-derivative of the PEG hydroxylic terminals. Among the reaction by-products, the hydroxylated biphenyl derivatives can be found. In other words, the reagent (A-PEG) dehalogenates the pollutant to form glycol ether and/or a hydroxylated compound and an alkali metal salt, which are water soluble by-products. This process can be operated in batch or continuous mode.

A variation of the A-PEG reagent is potassium hydroxide or sodium hydroxide/tetraethylene glycol, referred to as A-TEG, which is more effective on halogenated aliphatic compounds. In some K-PEG reagent formulations, dimethyl sulfoxide (DMSO) is added to enhance the reaction rate kinetics, presumably by improving the rates of extraction of the haloaromatic compounds. DMSO as a solvent increases the safety concerns as DMSO increases the ability of the contaminants to be absorbed through the skin.

A patented improvement of the APEG process designed specifically for the treatment of PCB containing transformer makes use of a non-alkali metal, (preferably a mixture of aluminium and titanium; iron, manganese, magnesium, nickel, palladium, silicon and zinc are also suitable), a long chain polyalkeneglycol and an alkali or alkaline earth metal hydroxide or alcoholate.

As far as contaminated soil is concerned, the glycolate dehalogenation process consists of five steps: preparation, reaction, separation, washing, and dewatering. During the preparation step, the contaminated waste (soil, for example) is excavated and sifted to remove debris and large objects such as boulders and logs. In the reaction step, the contaminated soil and the A-PEG reagent are blended in a reactor, mixed, and heated for four hours.

The resulting vapor from the heating process is collected and separated into water and gaseous contaminants by means of a condenser. The water can be used during a later step in the process and the gaseous contaminants are passed through activated carbon filters to capture the contaminants. Dehalogenation (A-PEG/K-PEG) is generally considered a stand-alone technology. However, it can be used in combination with other technologies. Treatment of the wastewater generated by the process may include chemical oxidation, biodegradation, carbon adsorption, or precipitation.

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 non-detectable levels at part per trillion sensitivity.

Limitations: Following EPA (US EPA, 540/S-93/s 506), and regarding the soil treatment, the disadvantages of the conventional A-PEG processes are that it often takes numerous cycles of the process to achieve the desired results, the process only effects partial dehalogenation, and the formation of dioxin and furans often occurs when the process is implemented.

5.1.3. Hydrodehalogenation

Process Description: The reductive dehalogenation of halogenated organics is an important and well known reaction frequently used in organic synthesis. It may be defined as the breaking of a single bond between a carbon atom and the halogen atom with the subsequent formation of a single bond between hydrogen and carbon:

$$C - X + H_2 \rightarrow C - H + HX$$

Where, $X = Cl, F, Br, I$

The rate at which the halogen-carbon bond may be reduced depends upon several factors:

- halogen type;
- structure of the molecule in the vicinity of the halogen atom;
- pressure, temperature

In general, based on a fixed molecular structure, the order in which the halogenated organics may be reduced is:

I > Br > Cl >> F.

The C-F system presents the biggest resistance to the hydrogenolysis due to its high energy of dissociation.

There are several available methods for the reductive dehalogenation of halogenated organics. Among these, the catalytic reductive dehalogenation by means of molecular hydrogen, and the one by means of hydrogen transfer, are the most studied for the dechlorination of PCBs.

Dehalogenation by means of molecular hydrogen: The reaction of halogenated aromatics with hydrogen results in the formation of the related unsubstituted aromatics compound and the halogen acid:

$$Ar\text{-}X \ + \ H_2 \ \rightarrow \ Ar\text{-}H \ + \ HX$$
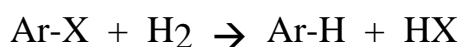
The reducing agent is the molecular hydrogen and the reaction may proceed only in the presence of a catalyst. The most commonly used catalyst are noble metals like platinum, palladium, linked with supports of fine grained $CaCO_3$, $BaSO_4$, C and the Raney-Nickel.

This is a widely applied process in the oil refining industry for the hydrogenation of crude oil. In some cases, oil refining companies have adapted their own plant of catalytic hydrogenation for the treatment of PCB wastes. The process works at high temperature and pressure (270-390°C; 14-70 atm.), as used in the crude oil processes.

With few exceptions, this process has not yet been developed on industrial scale for the treatment of PCBs, due to the high cost of the catalyst and low conversion rate observed.

Some new hydrodehalogenation processes using palladium as a catalyst work at atmospheric pressure. The catalyst, made by $PdCl_2$, is anchored to a N-vinyl-2-pyrrolidone support. The reaction operates at atmospheric pressure and 65°C, and is

strongly poisoned by the formation of HCl. 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 Raney-Nickel catalyst is usually slower than the palladium based ones, and requires 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.

Hydrodehalogenation by means of hydrogen transfer: In this process, the hydrogen molecule is transferred from the organic molecule to the halogenated compound, and thus the process is usually called "hydrogen transfer dehalogenation". Compared to the catalytic reduction with molecular H2, the hydrogen transfer reaction presents several improvements. First of all, as hydrogen donors are not gaseous compounds, this kind of process avoid the risk related to the use of the hydrogen gas and pressurized reactors.

The hydrogen transfer reaction is as following:

DH_2 + Ar-X → Ar-H + D + HX

Where, DH_2 = hydrogen donor, Ar-X = halogenated aromatics and   D = (hydrogen acceptors)

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

The reaction environment is quite complex, as the simultaneous presence of a matrix contaminated by PCB, a strongly basic aqueous phase, a phase transfer agent represented usually by a quaternary ammonium salt, a solid catalyst, a gaseous phase is usually involved.

A key aspect is the selection of a proper solvent, which may play a very sensitive role in the function of the type of contaminated matrix, and which may affect the effectiveness of the transfer of hydrogen between phases. The role of the phase transfer agent is to transfer reagents from one phase through the interface toward the other phase, in order to overcome the problem related to phase heterogeneity and allow the reaction to proceed.

A lot of research work has been performed in order to discover if the role of the base in the aqueous phase is limited to the removal of the chloridic acid produced during the dehalogenation reaction, or if other phenomena are involved in the process. In the literature, results concerning dehalogenation reactions using different bases (KOH, NaOH, Ca(OH)2 , Na_2CO3 , Mg(OH)2) are reported, showing that the catalytic activity is directly related to the base strength. Systems using less strong base require longer reaction times to allow for a complete dehalogenation.

Some reductive dehalogenation processes like the BCD (Base Catalyzed Dehalogenation) process are strongly based on the idea that the base plays a central role as the catalytic agent.

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. The Gas-Phase Chemical Reduction (GPCR) is based on gas-phase thermo-chemical reaction of hydrogen with organic compounds. At 850ºC 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.

Organics such as PCBs, PAHs, chlorophenols, dioxins, chlorobenzenes, pesticides, herbicides and insecticides are quantitatively converted to methane. Approximately 40% of the methane produced can be subsequently converted to hydrogen via the water shift reaction and the remaining methane can be converted to hydrogen in the catalytic steam reformer. Thus, the process can operate without an external supply of hydrogen.

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

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 at 35ºC by cooling the scrubber water using dual plate heat exchangers and cold water from an evaporative cooler.

This process is likely to be preceded by a thermal desorption unit when treating solid wastes. There is potential for the removal of organic contaminants from the solid material, as the thermal desorber will operate under a reducing hydrogen atmosphere, offering simultaneous destruction. Under a reducing atmosphere, the formation of dioxins is less likely to occur, although partial hydrogenation of more chlorinated molecules (eg OCDD to TCDD) may still occur and will depend upon the efficiency of the overall desorption and hydrogenation process.

The technology utilizes reduction chemistry rather than oxidation reactions typical to incinerators. By reforming contaminants in a hydrogen atmosphere, the possibility of forming dioxins and furans as by-products is greatly reduced. The off gases (primarily methane and hydrochloric acid) are held and analyzed prior to reuse or recycle thus ensuring that there are no uncontrolled emissions

Advantages

- 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

Process Description: The Base Catalyzed Dechlorination (BCD) process was developed based on the 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 pre-treatment step such as thermal desorption which yields a relatively small quantity of the 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 BCD patent (Rogers, 1991, US Patent 5,064,526) indicates that 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 distill from the mixture during treatment.

An alkali is added to the contaminated medium in proportions ranging from 1 to about 20 percent by weight. The amount of alkali required is dependent on the concentration of the halogenated or non-halogenated organic contaminant contained in the medium.

A hydrogen donor compound is added to the mixture to provide hydrogen ions for reaction with the halogenated and non-halogenated contaminants, if these ions are not already present in the contaminated material. The hydrogen donor compound may comprise of high boiling point solvent in which the alkali or alkaline earth metal compound is added, or it may include fatty acids, aliphatic alcohols or hydrocarbons, amines or other similar compounds. In order to activate these compounds to produce hydrogen ions, a source of carbon must be added, either in solution or in suspension. An inexpensive carbon source which is water soluble and suitable for use is a carbohydrate such as sucrose.

The mixture is heated at a particular temperature and for a time sufficient to totally dehydrate the medium. This may be performed at atmospheric or at reduced or elevated pressure. The water which is included in the aqueous solution allows homogeneous distribution of the alkali throughout the mixture and acts as a wetting agent and penetrant. When the water is removed from the medium during the dehydration step, the alkali is concentrated to a reactive state.

After dehydration, the medium is further heated to about 200°C to 400°C for a time sufficient to effect reductive decomposition of the halogenated and non-halogenated organic contaminant compounds, typically 0.5 to 2 hours. At this temperature, the carbon source (eg the carbohydrate) acts as a catalyst for the formation of a reactive

hydrogen ion from the hydrogen donor compound. This catalyzed reaction is represented by the following reaction formula:

R+M $\rightarrow$ (heated at 200 to 400°C, C) $\rightarrow$ R + H$^-$ + M$^+$
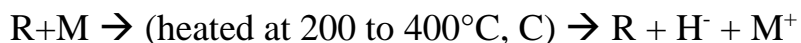
Where, R is the hydrogen donor compound, M is the metal compound, C refers to a source of carbon, for example a carbohydrate, and H is the hydride ion. The reactive hydride ion then reacts with the halogenated organic compounds contained in the contaminated medium according to the following reaction:

H+ R-X + M$^+$ $\rightarrow$ (heated ad 200 – 400°C) $\rightarrow$RX + R-H

Where R-X is the halogenated organic contaminant, X is the halogen atom and R-H is the reduced form of the contaminated compound.

Finally, the mixture is neutralized by the addition of an acid, preferably to a pH of 7 to 9. Depending on the nature of the feed material, the reagent additions and the site use, it may be possible for the treated material to be returned to the site if desired, although this may not be possible if the treated material is oily or has a high salt content.

Generally, oxygen will not adversely affect the BCD process and therefore air does not need to be excluded. When applied to the decontamination of hydrocarbon fluids, either aliphatic or aromatic, air needs to be excluded in order to prevent ignition of the hydrocarbon at the elevated temperature of the BCD reaction. This is achieved by passing nitrogen gas through the reaction vessel.

Performance

Test results show that the BCD process is able to reduce PCB from 100000 mg/kg to below detectable limits in approximately 2 hours (Rogers, 1991). Test results reported by the license owner reported a decrease in concentration from up to 300000 ppm to under the detection limits in 90 minutes.

A sample of contaminated soil containing 2,200 mg/kg of Aroclor "1260", 1000 mg/kg of Aroclor "1242", 1000 mg/kg of PCP, 1000 mg/kg of dieldrin, 1000 mg/kg of lindane and 500 mg/kg of BCD 2phenylnaphthalene, was treated by this process and the contaminants reduced to less than 1.0 mg/kg each. The 2phenylnaphthalene was also reduced to a cyclic hydrocarbon (Rogers, 1991).

The process mainly involves chlorine stripping. In treatment of chlorinated aromatic hydrocarbons the removal of chlorine atoms results in an increased concentration of lower chlorinated species (eg higher congeners are replaced by lower congeners). This is not a problem with contaminants such as PCBs. However, with constituents such as dioxins the lower congeners (eg TCDD) can have a higher toxicity than the more highly chlorinated congeners (eg OCDD). Therefore the process must be monitored to ensure that the reaction continues to completion.

In the case of treatment of PCBs and PCB contaminated oil, treatment will typically reduce the PCBs to less than detection limits (0.1 mg/kg total PCBs for the lower congeners, and 0.01 mg/kg for the higher congeners) if sufficient reaction time is allowed. Given that the process is a batch operation, it is possible to allow the reaction to proceed until the required level of destruction has been confirmed.

5.2. THERMAL DESTRUCTION OF PCBS

5.2.1. INCINERATION

In general, the objective of the incineration process is to reduce the waste volume and to simultaneously destroy the hazardous contaminant contained in the processed waste. In the case of disposal of PCB waste, the objective to destroy the toxic fraction of the contaminated waste (the PCBs themselves) is however prevalent over the objective to reduce the volume of waste;

One of the most important things to be considered in the disposal of PCB wastes is the chemical and physical composition of the waste stream. The chlorine content of the waste stream needs to be carefully controlled to ensure that the emission of PCDD/F are kept under the 0.1 ngTeq/m^3 level as per the minimum BAT requirement. Usually, waste with no more than 3% content of chlorine are burnt in industrial waste incinerators, although specially designed incinerators may burn liquid waste with high concentration of PCBs, up to 15% - 20%.

If the wastes to be treated are made homogeneous in term of their physical composition (e.g., physical state, size, thermal content, moisture level, amount of non-combustible fractions, etc.), the destruction efficiency of the process may be greatly improved and the management of the air pollution control system can be facilitated. This could allow a better environmental performance of the process coupled with a significant reduction of the operational costs. Therefore a sound pre-treatment system is necessary.

As incineration is usually not economically viable below a certain capacity, incineration plants are usually large facilities requiring a significant portion of land. Thus an incinerator plant for PCB must always be thought as a part of a hazardous waste disposal platform, where a complete system for waste characterization, pre-treatment, proper mixing with other waste stream, and an up-to-date system for air pollution control and on-line monitoring is in place. Incineration still represents in some cases the first choice treatment technology for the destruction of PCB, however some limitation should be considered when adopting this technology:

- It does not allow the recovery of valuable resources (like dielectric oil), with the exception of the chemical energy which may be partially recovered as thermal or electrical energy;

- If not properly operated, incineration of PCB wastes may produce PCDD and PCDF in the exhaust gases. Exhaust gases may also contain other contaminants like heavy metals, particulates, Nox, SOx. Hcl which need to be recovered or abated.

- The cost of the air pollution control and monitoring systems may represent a significant fraction of the investment cost, making incineration economically feasible only for large capacity plants.

Process details

Incineration is the chemical reaction of oxygen (oxidation) with a combustible material. A great advantage of the incineration process is their highly non specificity: 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**: 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 oxidizing 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 oxidizing agent at approx. 400 – 700 °C. Gasification of the carbonaceous residues is the reaction of the residues with water vapor and CO2 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 oxidized, depending on the selected incineration method, at flue-gas temperatures generally between 800 and 1450 °C.

To achieve good burn-out of the combustion gases, a minimum gas phase combustion temperature of 850 °C and a minimum residence time of the flue-gases, of two seconds after the last incineration air supply have been established in legislation (Directive 2000/76/EC and earlier legislation).

In the case of PCB incineration, the recommended values for the operational parameter are:

- minimum residence time of the flue-gases of 2 seconds above 1200°C at 3% O_2 content, or 1.5 sec at 1600°C and 2% di O_2 content;

- combustion efficiency greater than 99%;

It is also recommended to adopt technologies for the online monitoring of the PCB feeding rate and for the on-line monitoring of O_2, CO_2, CO, NOX, SOx, HCl, PM10 at the stack. Periodical measurement of the concentration of PCDD/PCDF, PCB, PAH and heavy metals at the stack should be also performed. Moreover, systems for the control of HCl emissions must be adopted.

The main process modules which are usually present in an incineration site are:

- Waste reception facilities (parking, weighting, registration, archiving)
- Waste analysis laboratory
- Temporary storage for incoming wastes
- Waste pre-treatment
- Incineration plant (including waste loading system)
- Energy recovery systems (steam boilers, turbines for electricity production, co-generation systems, etc.)
- Waste water control and treatment plants
- Environmental monitoring systems (air, water)
- Inertization plant for the treatment or contaminated ash
- Landfill for ash disposal and other solid waste disposal.

In the case of plants dedicated to the destruction of halogenated waste, a module for recovering / recycling of chlorine, in the form of HCl, should be considered.

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 to 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 minimize 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 combustibles and a continuous ash removal. The residence time of solids is easy to manage, and the need for waste pre-treatment is very low. Disadvantages consist in the fact that the 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.

For the purpose of hazardous waste destruction, rotary or drum kilns may be equipped with post-combustion chamber and with injector for the management of pumpable wastes.

The post combustion chambers are generally designed to meet the residence time required by the regulation (EC Directive 2000/76/EC in Europe) for flue gases and for directly injected liquid wastes.

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^2. It is divided in to 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 of around 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_2O_3 and SiO_2

- **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 the 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 to 80-95°C in less than 1s. The cooling and absorption medium is water.

- **NaOH absorbtion chamber**: The NaOH absortion tower are based on counter or co-current spraying of a NaOH solution, for the neutralization of Chlorine.

- **Fabric filters with lime and activated carbon injectors:** The fabric filter for the removal of fly ash should be equipped with injectors of lime and activated carbon. This 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 to 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 sufficient 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 electrodialysis, 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 presents 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 pre-treatment 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.

Emissions to air due to the incineration of hazardous wastes

In the following table data concerning the measured emissions of Hazardous Waste Incineration plants in Europe are reported

Parameter mg/Nm³ unless stated	Yearly average		
	Minimum	Maximum	Average
HF	0.01	<1	0.3
TOC	0.01	6	1.5
O_2 (%)	8	13.66	11.0
NO_x	44.4	<300	139
Dust	0.075	9.7	1.69
HCl	0.25	8.07	1.56
SO_2	0.1	22.7	7.8
Hg	0.0004	0.06	0.01
Cd +Tl	0.00014	0.046	0.01
Sum metals	<0.004	0.84	0.2
PCDD/PCDF (ngTEQ/Nm³)	0.0003	<0.1	0.038
CO	3	26	12.9

Table 3.21: Survey data of the annual average emissions to air from hazardous waste incinerators in Europe
[41, EURITS, 2002]   .

5.2.2.   PLASMA

Scope: The Plasma technology may be used to destroy basically any type of liquid or solid waste. There are no limits in the concentration of POPs or other waste that can be destroyed by this technology, as plasma may operate at very high temperature. However plasma is more cost-effective for concentrated solution to pure POPs stream. Incineration in conventional plants would require mixing with fuel or other waste stream. The plasma technology originated from industrial technologies which have been initially consolidated in industrial manufacturing, like electric arc furnaces for the production of steel from steel scraps or pig iron, CAD steel cutting, etc. Although it has been reported that the main shortcoming of plasma is its high energy consumption, due to the small volume of the system that need to be heated compared to incinerators, to the very fast shut down and turn on cycles, and to the fact that plasma may destroy pure stream of POPs without need of diluting them with fuels or other waste, for pure POPs stream plasma may be much more cost effective and less energy consuming than other technologies. Plasma is moreover the only technology that can process hazardous waste like ashes coming from incineration of hazardous waste, or asbestos.

Process Description: Thermal plasma is a high temperature, partially or completely ionized gas. Thermal plasma is usually generated by an electric current (alternate at high frequency or continuous) passing through the gas; the resistivity energy is

dissipated by the gas which, with the increase in temperature, becomes 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 offers several advantages for the elimination of toxic wastes:

- The use of electricity for the production of heat eliminates or greatly reduces the use of air for the combustion process; if an inert gas is used for generating the plasma, this renders it to be a pyrolysis process leading to the destruction of waste without oxidation.

- The high energy density and the high temperature allows 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 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 is rather inefficient from the thermodynamic point of view. This shortcoming however becomes negligible for the treatment of waste that is inert and decomposes 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 of 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 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 processes as a reagent with exhaust gas generated by the thermal destruction process. In some plants, exhaust gas made of carbon and hydrogen is made by reacting with a stoichiometric amount of oxygen to generate a CO. CO and H2 are subsequently recovered or burnt in a flare, to generate CO2 and H2O.

4) **Waste feeding system:** Depending on the type of waste, waste feeding may take the form of an injection system for 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 arc:** 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 electrode 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 arc:** In the transferred arc, 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 m3/hr to tenths of m3/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: made by spraying the gas with an alkaline solution in the quencher.

c) Other flue gas treatment components: 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 feed, 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 in compliance with the regulatory limits. Water treatment system may be composed of evaporator modules or 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 is 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 NOx, SOx, O2, dust, HCl;

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

Key Operational Parameters

In the following table, the key operational parameters for three types of plasma technologies commercially available are listed.

Parameter	CSM Mobile Plasma for solid waste	PACT™ System for mixed waste	PLASCON liquid waste unit
Main scope of the plant	Mainly pulverized or granulated solids (asbestos); suitable for semisolid waste or liquid waste.	Solids in drums; suitable also for semisolid, pulverized or granulated waste	Only liquids and gases
Capacity (t/hr)	0.3	0.2 (based on the duration of the whole cycle)	0.135 (for pure PCBs)
Maximum power	1MW		150KW
Max current and voltage	2000A, 500V		
Type of plasma	Transferred arc, computerized design plasma torches	Multimodal torch (nonTransferred for heating up, transferred for melting waste)	Non transferred arc, in flight destruction of waste.
Type of reactor	Cylindrical reaction chamber (1mx1m)	Centrifugal chamber (1m^3)	"In flight" tube.
Batch / continuous process	Batch (continuous for liquids)	Continuous	Continuous
Operation temperature in the destruction zone	Over 1700°C	1650°C	3100°C
Flue gas flowrate (m^3/hr)	500 Nm^3/h		0.5 Nm^3/hr
Mobile /	Transportable	Fixed	Mobile

Transportable / Fixed			

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 means 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 Ce is the equilibrium concentration of PCBs in the dielectric oil, C0 is the initial concentration of PCBs in the dielectric oil, Vp is the interstitial volume of the porous material, C1 is the concentration of PCBs in the clean oil, and Vs is the internal volume of the transformer. To reach equilibrium concentration could require, under 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 the cleaned oil several times etc. When feasible, the most economical way of performing retrofilling is however to perform an accurate draining of the oil, and then to place again the transformer in use; after a few months, the PCBs concentration in the transformer is checked, and if necessary the retrofilling process is repeated. The process is repeated until the PCBs concentration in the dielectric oil remains stable under 50 ppm.

It is quite evident that retrofilling is only suitable for transformers with medium – low concentration of PCBs in the dielectric oil, for the following reasons:

- Transformers with a high PCBs concentration require several cycles for reducing their contamination to under 50 ppm required by the Stockholm convention; on the basis of the formula reported above, and assuming an interstitial volume of the porous material of around 15% of the internal free volume of the transformer, treating a transformer filled with a commercial PCB based dielectric oil would require at least 6 treatment cycles to achieve a decontamination of PCBs under 50 ppm;
- The oil replaced at each retrofilling cycle has to be destroyed or chemically dehalogenated, and new oil has to be procured. This cost is sustainable only for transformers which still have a high residual value and are not highly contaminated.
- Transformers designed to work with pure PCBs oil, once filled with mineral oil, may need to be derated due to the different dielectric properties of the mineral oil compared to the PCBs oil.

Figure 4: Decontamination trends with retrofilling, starting from different concentrations. For pure PCBs, at least 6 cycles are required to bring PCBs contamination below 50 ppm.
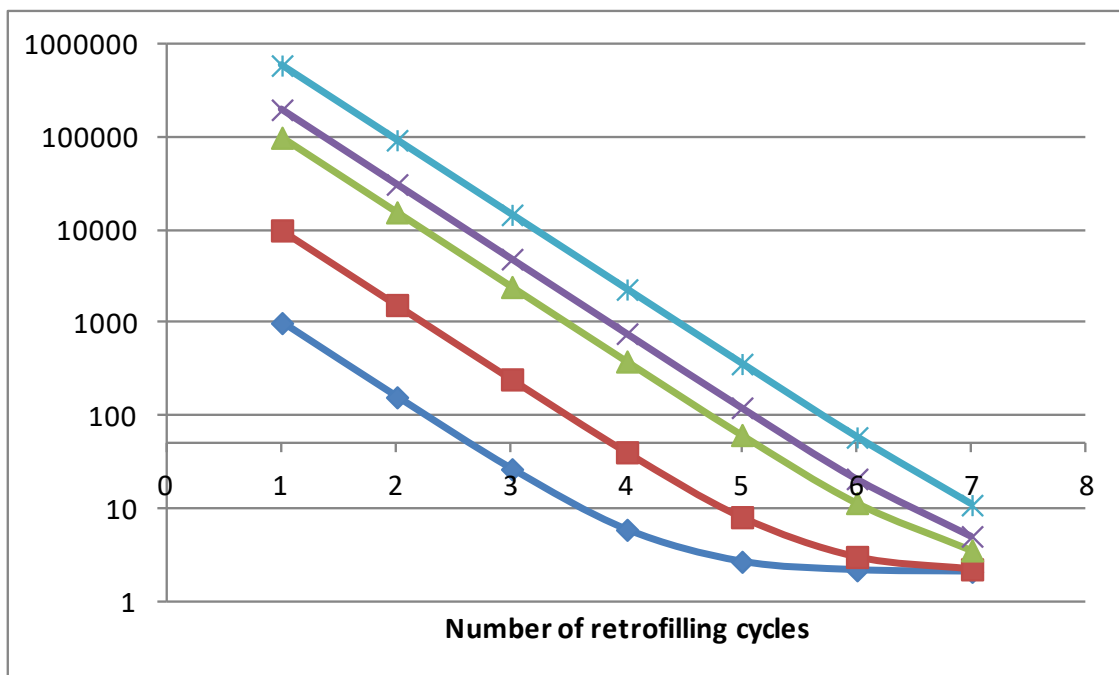
6.2. SOLVENT WASHING

Process Description: 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 to the compound and the two solvents. For instance, the Kow partition coefficient is the ratio at the equilibrium between the concentrations of the compound in octanol and water: Kow = log (Coct/Cw). PCB compounds are characterized by a high Kow value and a low solubility in water, which means that these compound are very lipophilic and hence hardly extracted from contaminated media like oils or soils with high O.C. content. In order to chemically extract PCBs from contaminated oil 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 being conceptually simple, its application may be quite complex, and different firms have developed patented solutions 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 the decontamination processes.

Solvent extraction may be a good technology for the decontamination of contaminated soils and contaminated equipment at its end of life; however, as it is not a stand-alone technology, it requires both pre-treatment and the subsequent destruction of PCBs, which have to be carried out with the proper BAT/BEP.

Process details: 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.

The solvent extraction process always requires a pre-treatment step. If the material to be decontaminated is an "end of life" transformers or capacitors, the oil contained in these equipment must be drained and stored for subsequent treatment; the copper windings must be opened and cut with the proper technology; all these operation

must be carried out using equipment and procedures fulfilling high safety and pollution prevention measures.

When this technology is applied for the decontamination of soil, it generates three main process streams: the extract containing concentrated contaminants, the treated soil or sludge, and the separated water. The extract contains contaminants concentrated into a smaller volume, which requires further treatment such as incineration or dehalogenation.

In the case of contaminated soil or wastes, the treated solids may need to be de-watered, forming a dry solid and a separate water stream. The volume of product water depends on the inherent dewatering capability of the liquid-solid separation process, the specific water requirement for feed slurry, and initial soil or sediment water content.

The water should be analyzed to determine if treatment is necessary before discharge. Since the solvent is an organic material, some residue may remain in the soil matrix. This can be mitigated by solvent selection, and if necessary, an additional separation

Near-critical fluid/liquefied gas extraction is similar to standard solvent extraction. The difference is that the solvent is near its thermodynamic critical point (the temperature and pressure at which the liquid and vapor phases of the solvent in equilibrium with each other becomes identical, forming one phase). As a fluid approaches its critical point it increasingly exhibits the diffusivity and viscosity characteristics of a gas, while continuing to exhibit the solvent characteristics of a liquid. Thus a solvent near its critical point can effectively penetrate a soil matrix with rapid mass transfer and remove pollutants. Near-critical fluid/liquefied gas extraction processes generally operate at elevated pressure. Processes have been designed to handle either solids or liquids.

Critical Solution Temperature processes use extraction solvents in which solubility characteristics can be enhanced by changing the fluid's temperature. For the PCBs decontamination purposes CST solvents include those binary (liquid-liquid) systems which exhibit an upper critical solution temperature, a lower critical solution temperature, or both.

For such systems, mutual solubility of the two liquids increase while approaching the CST. At or beyond the CST the two liquids are completely miscible in each other.

This may represent a great advantage for the treatment of contaminated soil or sludge with a significant fraction of water content.

Performance: The extraction process between oil and DMF (Dimethyl-formamide) Rimbach (1982) Heylin (1983) and between oil and the methyl ethers of diethyleneglycol, (Rouse et al., 1983), starting from a concentration of 100 ppm of PCB in oil, after a single step reduced at 1/3 the residual concentration in the oil; the solvent is distilled and recycled, and the volume of the contaminated fluid is reduced to 1/10.

Experimental tests with soil contaminated with Aroclor 1016 (Majid, et al., 2002) (initial concentration of 800-1200 mg/kg) and a mixture of hexane and acetone used as solvent yielded, after two cycle of extraction, a residual concentration in soil of around 50 mg/kg.

Preliminary findings from the SITE demonstration of the Terra Kleen technology: PCB Aroclor 1260 concentrations were reduced from an average of 144 milligrams per kilogram (mg/kg) in untreated soil to an average of 1.72 mg/kg in treated soil. The average removal efficiency was 98.8%.

6.3. THERMAL DESORPTION AND VACUUM ENHANCED THERMAL DESORPTION

Following US EPA, (U.S. EPA Engineering Bulletin on Thermal Desorption Treatment, Superfund, EPA/540/S-94/501, February, 1994), thermal desorption may 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 oxidise 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 proved that it can produce a final contaminant concentration level below 1 mg/kg for the target contaminants identified.

A shortcoming of this technology lies in the high energy requirement, and in the presence of gaseous effluents which need to be monitored and treated. All thermal desorption systems require treatment of the off-gas to remove particulates and contaminants. Particulates are removed by conventional particulate removal equipment, such as wet scrubbers or fabric filters. Contaminants are either removed through condensation followed by carbon adsorption, or they are destroyed in a secondary combustion chamber or a catalytic oxidizer. Thermal desorption should not be considered as an incineration process, in the sense that wastes are not combusted, and the thermal energy is only used for the phase transfer of the PCB; the investment and operating cost of devices for the off gas treatment, together with the need to complete – within the same plant or in a different one - the destruction of the contaminant extracted may represent an obstacle to these technologies.

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 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.

Applicability: The target contaminant groups for LTTD systems are halogenated and non-halogenated VOCs. The technology can be used to treat SVOCs and PCBs contaminated soil when high temperature and long residence time are ensured. Batch thermal desorption under vacuum is used to remove PCBs from metal scraps or transformer carcasses.

Limitations: The following factors may limit the applicability and effectiveness of the process:

For PCBs contaminated soil:

- Dewatering may be necessary to achieve acceptable soil moisture content levels
- Highly abrasive feed potentially can damage the processor unit
- Heavy metals in the feed may produce a treated solid residue that requires stabilization
- Dust and organic matter in the soil increases the difficulty of capturing and treating off-gas.

For PCBs contaminated equipment:

- Large transformers need to be dismantled before being treated with thermal desorption under vacuum, due to size limitation of batch desorption chambers;
- Thermal desorption of PCBs contaminated equipment is in general not economically sustainable for small size equipment which can be treated by a simple pre-treatment process (shredding) followed by incineration.

7. INTEGRATION OF TECHNOLOGIES

Retrofilling, solvent washing and thermal desorption cannot be considered technologies for POPs disposal, as these technologies have an objective of only the physical transfer of PCBs without destroying them.

Therefore these technologies have to be integrated with disposal technologies.

Retrofilling is very often the only chance for the treatment of large PCBs transformers with low-medium contamination of PCBs. The large PCBs amount of oil generated by the multiple-cycle retrofilling treatment of transformers calls for close integration with PCB destruction technologies. The choice between incineration of the contaminated oil and dehalogenation followed by regeneration of oil largely depends on economic constraints, like the cost of dehalogenation (which is mainly driven by the cost of metallic sodium), the cost of incineration, and the cost of new dielectric oil. There is always the risk that private or small PCBs owners may find it convenient to sell contaminated oil without checking it for PCB content, in order to get some revenue for compensating the cost of new oil for retrofilling transformers. If the cost of dielectric oil is high, it is likely that the options leading to its environmentally safe regeneration would be more competitive; the same could be obtained by financially supporting ESM technologies for the destruction of PCBs and the regeneration of oil.

8. CONSIDERATIONS RELATED TO THE SELECTION OF THE SITE FOR PCB DISPOSAL

The selection of the site for the establishment of PCBs disposal facility should be based on logistic, infrastructure, environmental, permitting considerations.

Logistic aspects: In the selection of the site, proper consideration must be given to the distance to sites where PCBs equipment is located, including areas for the

intermediate storage of PCBs. Transportation cost is an important component of the overall handling and disposal of PCBs equipment; moreover, transportation of PCBs should rely as much as possible on well-maintained transport infrastructures. The establishment of a disposal facility should therefore always include a transportation plan and an assessment of transportation infrastructures; the needs for establishing temporary storage areas for PCBs equipment also needs to be properly assessed.

Infrastructure and utilities: Depending on the technology selected, the availability of utilities and infrastructures must be ensured. Availability of utilities like industrial and potable water, electricity, steam, must be properly assessed at the light of the needs of the technology. For instance, the establishment of a plasma facility would require a reliable and powerful connection to the electric network, capable to bear the peaks of energy required at the startup of the facility; chemical dehalogenation plants require in general the availability of steam, that if not available as utility, must be generated on site; incinerators would require availability of large amount of water for quenching and cooling, etc.

Environmental aspects: Environmental constraints must be considered from both the side of the impact of the plant on the environment, and on the risk associated to extreme meteorological or natural events (floods, storm, lightning, earthquakes, atmospheric precipitation, etc.). Typically, both aspects are covered under a sound Environmental Impact Assessment analysis. Considering the hazard associated with the storage, handling and disposal of POPs, carrying out of an Environmental Impact Assessment covering the environmental criteria for selecting the site based on UN standards is considered mandatory.

Permitting considerations: Rules concerning the minimum distance from water bodies, populated areas, and protected areas must be obviously considered when selecting the site for establishing a disposal facility.

Public consultation and public perception: The involvement of the public by means of formal public consultation and proper awareness raising campaign since the early stage of the project is recommended.

9. 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 is extremely important, when drafting technical specification, to set for these tests only requirements and standard which are SMART, i.e. Specific, Measurable, Attainable, Relevant and Time Bound. For instance, one common requirement is that the plant has to ensure an availability of a certain percentage over time (for instance, at least 18 hours per day for at least 230 days/year). Unfortunately, compliance with this type of requirement can be reliably verified only after some years of operations. Common specifications are also may be that "core component of the equipment must ensure duration of certain number of years". This second requirement, though reasonable, cannot be part of any no-load test or proof of performance test, but must be inferred only on the basis of a statistically significant data base of similar plants or materials.

Therefore, in defining criteria for requirements or standards that, 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 indicators of an availability of 18/24 over 230 days/year.

Setting attainable target value for DE, DRE, and decontamination or cleanup target is also a key aspect in planning tests. Asking the supplier to demonstrate unreasonably low target concentrations or DE values, although attractive from the point of view of communication and public acceptance, may be dangerous as would expose the technology to a significant risk of failure; even if such low values are fulfilled, the extreme conditions under which the plant should run for attaining unreasonably low values may be not representative of the ordinary operational conditions. Target values for tests should be therefore always be based on sound scientific considerations.

9.1.   NO LOAD TEST

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 temperature, like incinerators or thermal desorber, necessary activities for the preparation of refractory material to

high temperature by means of progressive heating under programmed temperature ramps must be completed before the no-load runs.

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 hydraulic and pneumatic systems
- Complete test of fuel system 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.

9.2.   PROOF OF PERFORMANCE TEST

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 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 of 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