

# C6890 Technologie ochrany prostředí

## III. Technologie sloužící pro zajištění čistoty ovzduší

### III.3 Moderní trendy v oblasti zajištění čistoty ovzduší

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Č	Název přednášky	Obsah přednášky
III.	Technologie sloužící pro zajištění čistoty ovzduší	III.3 Moderní trendy v oblasti zajištění čistoty ovzduší

# BAT/BEP - Definitions

## Best available techniques (BAT)

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:

# BAT/BEP - Definitions

- ↪ **Techniques** includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;
- ↪ **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
- ↪ **Best** means most effective in achieving a high general level of protection of the environment as a whole;

# Proposed requirements for sound disposal of POPs

**Destruction and/or irreversible transformation of POPs wastes must achieve a destruction efficiency (DE)/ destruction and removal efficiency (DRE) of 99.9999%**

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OPEN-ENDED WORKING GROUP OF THE BASEL CONVENTION ON THE CONTROL OF TRANSBOUNDARY MOVEMENTS OF HAZARDOUS WASTES AND THEIR DISPOSAL First session Geneva, 28 April to 2 May 2003  Item 5 (d) of the provisional agenda*		
DRAFT TECHNICAL GUIDELINES ON THE ENVIRONMENTALLY SOUND MANAGEMENT OF PERSISTENT ORGANIC POLLUTANTS AS WASTES		

# Levels of destruction and irreversible transformation

Recognizing the following considerations:

- (a) Both **destruction efficiency (DE)** and **destruction removal efficiency (DRE)** are a function of the initial POP content and do not cover formation of unintentionally produced POPs during destruction or irreversible transformation;
- (b) **DE** is an important criterion for helping to assess technologies for destruction and irreversible transformation, but can be difficult to measure in a reproducible and comparable manner, especially on a regular basis;
- (c) **DRE** considers only emissions to air;
- (d) **BAT and BEP** set safe design and operating conditions, including expected destruction efficiencies, in particular circumstances on a technology by technology basis;

# Levels of destruction and irreversible transformation

- (e) **BAT and BEP** have not been identified for all disposal methods;
- (f) **Existence of** pertinent national legislation and international rules, standards and guidelines;
- (g) **Lack of knowledge and data;**

# Levels of destruction and irreversible transformation

The following provisional definition for levels of destruction and irreversible transformation, based upon absolute levels (i.e., waste output streams of treatment processes) should be applied:

(a) Atmospheric emissions:

PCDDs and PCDFs: 0.1 ng TEQ Nm<sup>-3</sup>;

All other POPs: pertinent national legislation and international rules, standards and guidelines, examples of pertinent national legislation can be found in annex II;

Determined according to national or international methods and standards.

TEQ as referred to in annex C, part IV, paragraph 2, of the Stockholm Convention, but only for PCDDs and PCDFs.



# Levels of destruction and irreversible transformation

Calculated on the basis of the mass of the POP content within the waste, minus the mass of the remaining POP content in the gaseous, liquid and solid residues, divided by the mass of the POP content within the waste, i.e.,

$$DE = (\text{POP content within waste} - \text{POP content within gas, liquid and solid residual}) / \text{POP content within the waste}$$

# Levels of destruction and irreversible transformation

Calculated on the basis of mass of the POP content within the waste, minus the mass of the remaining POP content in the gaseous residues (stack emissions), divided by the mass of the POP content within the wastes, i.e.,

$$\text{DRE} = (\text{POP content within waste} - \text{POP content within gas residual}) / \text{POP content within the waste.}$$

TEQ as referred to in annex C, Part IV, paragraph 2 of the Stockholm Convention, but only for PCDDs and PCDFs.  
Nm<sup>3</sup> refers to dry gas, 101.3 kPa and 273.15 K.  
Standardization at 11 per cent O<sub>2</sub>.

# Levels of destruction and irreversible transformation

- (b) **Aqueous releases:** pertinent national legislation and international rules, standards and guidelines, examples of pertinent national legislation can be found in annex II;
- (c) **Solid residues:** POP contents should be below the low POP contents defined in section A above of this chapter.

However, if the POP content of unintentionally produced PCDD/PCDFs is above the low POP content defined in section A, the solid residues should be treated in accordance with section IV.G.

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

# Criteria for determining best available techniques

1. The use of **low-waste technology**
2. The use of **less hazardous substances**
3. The furthering of **recovery and recycling** of substances generated and used in the process and of waste, where appropriate
4. **Comparable processes**, facilities or methods of operation which have been tried with success on an industrial scale
5. **Technological advances and changes** in scientific knowledge and understanding
6. **The nature, effects and volume of the emissions** concerned

# Criteria for determining best available techniques

7. The commissioning dates for new or existing installations
8. The length of time needed to introduce the best available technique
9. The consumption and nature of raw materials (including water) used in the process and energy efficiency
10. The need to prevent or reduce to a minimum the overall impact of the emissions on the environment and the risks to it
11. The need to prevent accidents and to minimise the consequences for the environment
12. Information published by public international organisations.

# Stockholm Convention on POPs

- ↪ Parties are to take measures so that POPs wastes are:  
“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 ...” (Article 6, L (d) (ii))
- ↪ Further, measures are to be taken so that POPs wastes are:  
“Not permitted to be subject to disposal operations that may lead to recovery, recycling, reclamation, direct reuse or alternative uses of persistent organic pollutants.” (Article 6 (d) (iii))

# Destroying technologies for POPs

## Based on oxidative processes

- ↪ High-temperature incineration
- ↪ Cement kilns
- ↪ Super-critical water oxidation
- ↪ Molten salt oxidation
- ↪ Electrochemical oxidation
- ↪ Advanced oxidative process

# Destroying technologies for POPs

## Based on reductive processes

- ↪ Catalytic hydrogenation
- ↪ Solvated electron technology
- ↪ Sodium reduction
- ↪ Dehalogenation processes
  - ❖ Base catalyzed dechlorination
  - ❖ Alkaline polyethylene glycolate (APEG) process
- ↪ Gas-phase chemical reduction
- ↪ Molten metal pyrolysis
- ↪ Ball milling



# Non-combustion technologies

## True non-combustion

- ↪ Reductive
- ↪ w/o oxygen
- ↪ Reduction with hydrogen and donors of hydrogen
- ↪ Reduction with metals and other reductants
- ↪ Mediated Electrochemical Oxidation

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## Alternative air oxidation

- ↪ Flameless
- ↪ Pyrolysis
- ↪ Indirect
- ↪ High temperature air oxidation: molten media, SCWO, and plasma arc technologies

# Destroying technologies for POPs

## Based on other processes

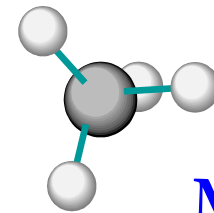
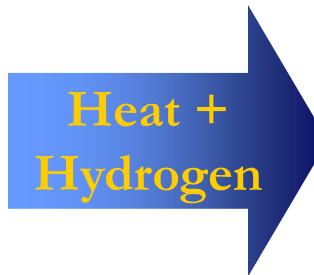
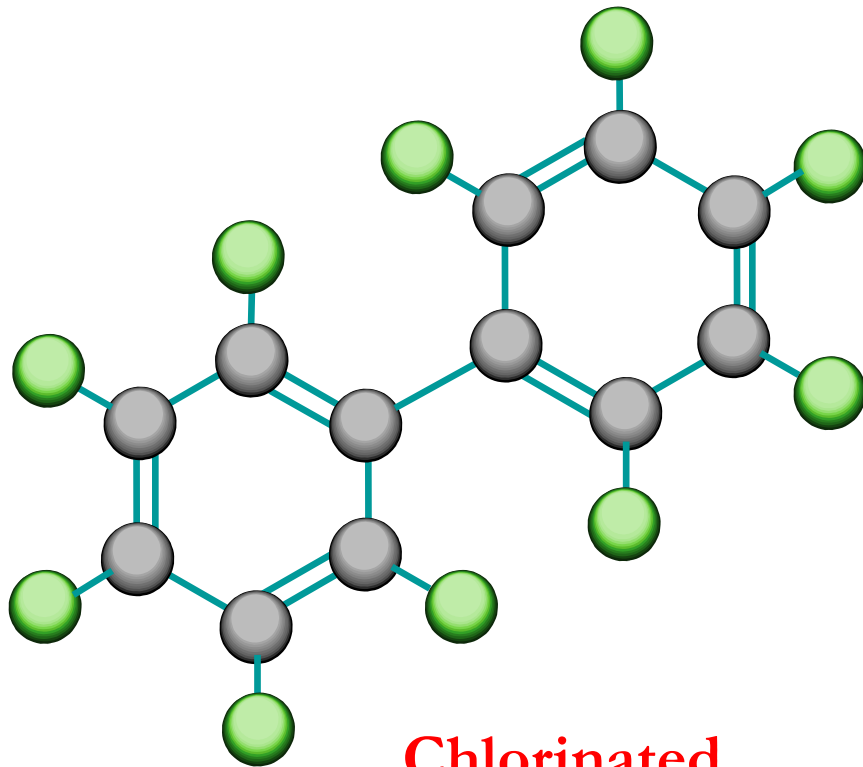
↪ Plasma arc

↪ Photochemical degradation

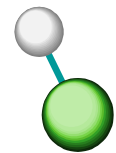
# What is „non-combustion technology“?

- ↪ **Decomposition of substances in the absence of oxygen**
- ↪ **Decomposition does not proceed in flame**
- ↪ **Decomposition proceeds at temperature lower than at combustion and plasma technologies**

# Gas-Phase Chemical Reduction of PCBs

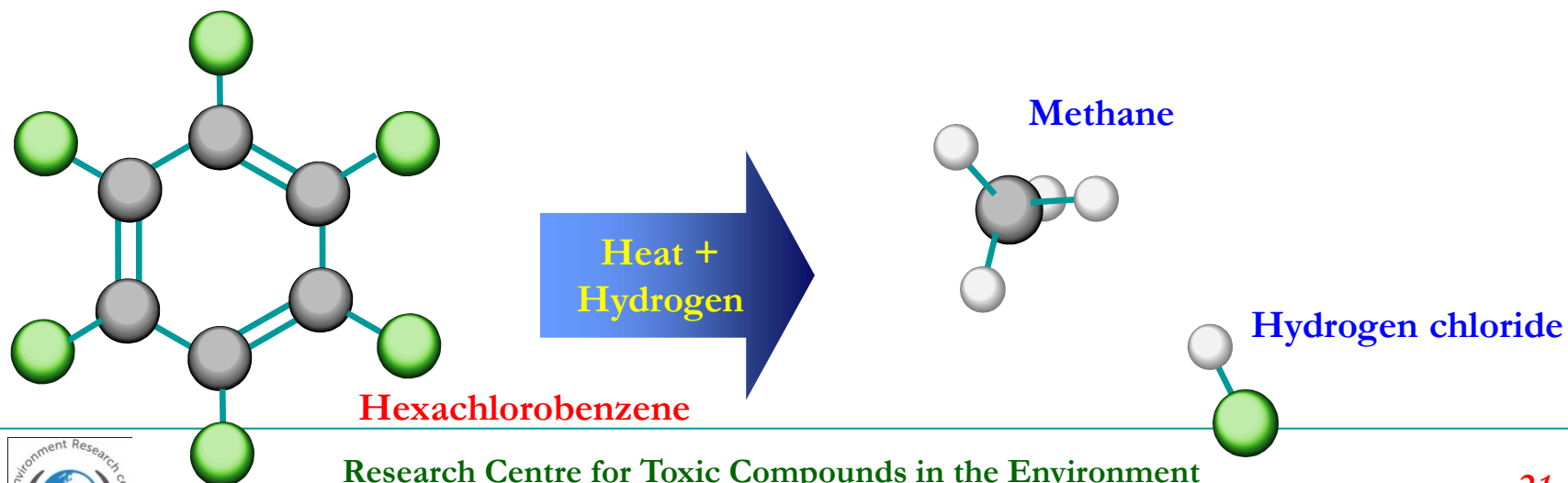
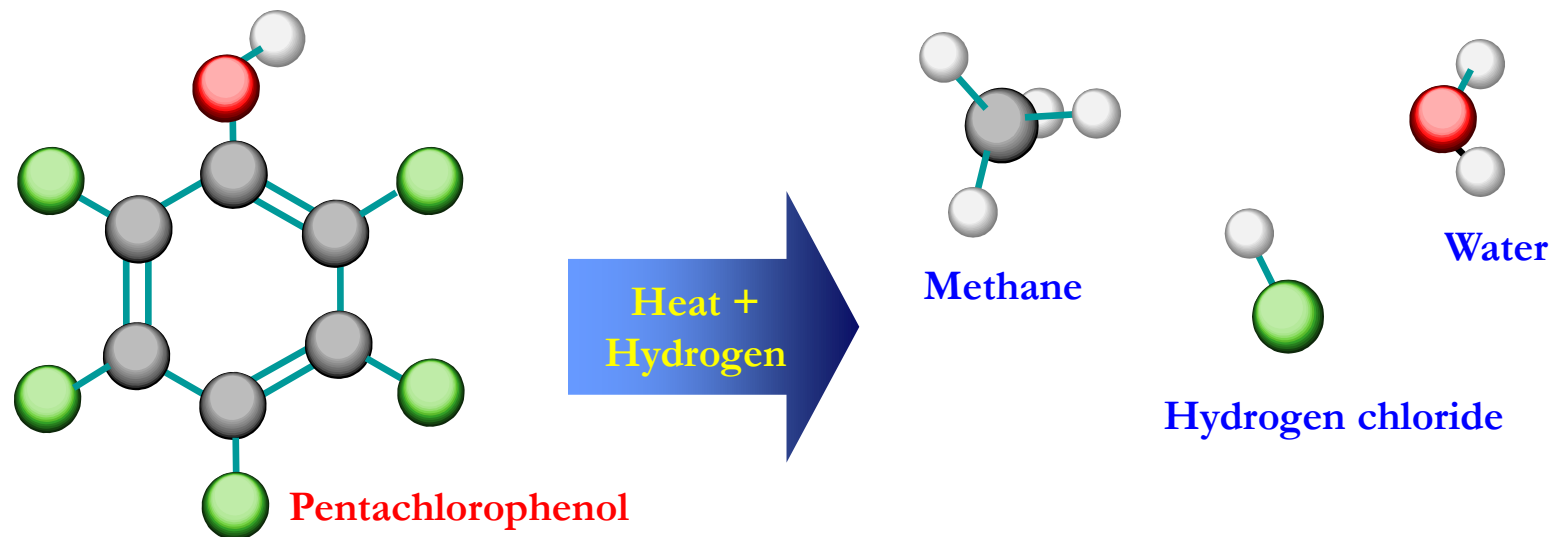


**Methane**



**Hydrogen chloride**

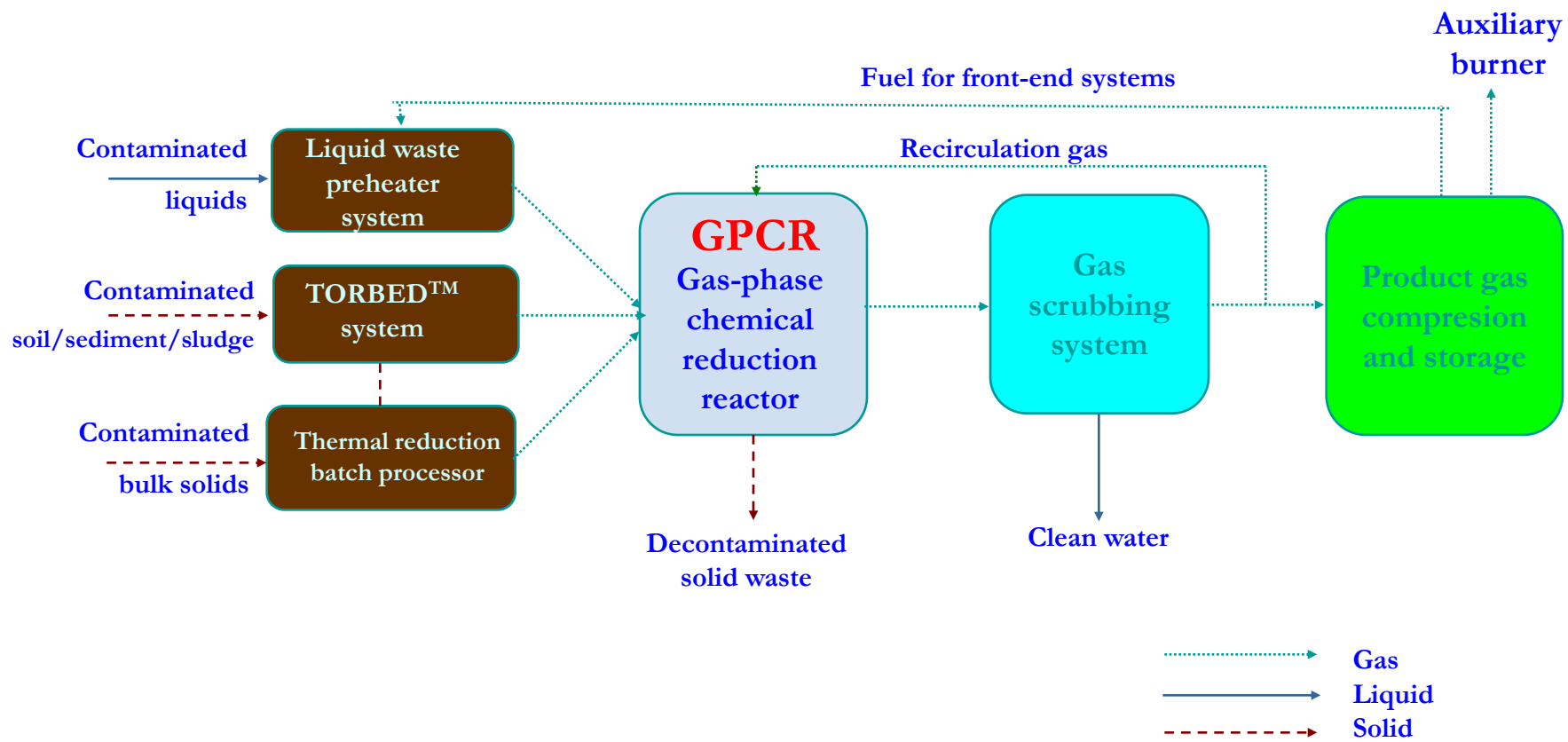
# Gas-Phase Chemical Reduction of PeCP and HCB



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# Gas-Phase Chemical Reduction Process Block Flow Diagram



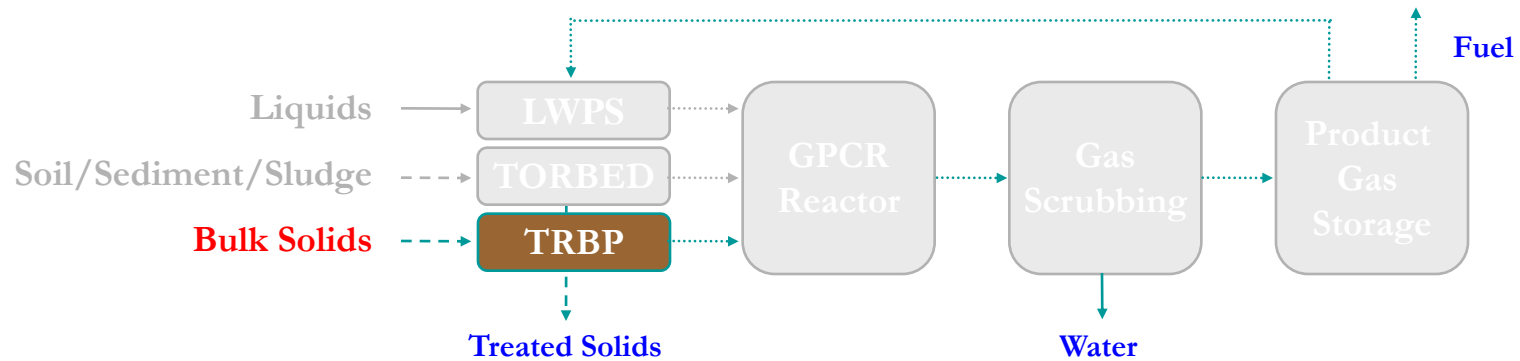
# Gas-Phase Chemical Reduction

Waste Matrix	Front-End Equipment
<b>Bulk Solid Waste</b> - electrical equipment, drummed waste, wood pallets, rubble, miscellaneous solids	<b>TRBP (Thermal Reduction Batch Processor)</b>
<b>Liquid Waste</b> - PCB oil, oily waste, watery waste	<b>LWPS (Liquid Waste Preheater System)</b> for homogeneous liquids with low suspended solids content; <b>TRBP</b> for all other liquids
<b>Granular Solid Waste</b> - soil, sediment, sludge	<b>TORBED</b>

Desorbed or volatilized organic contaminants from the front-end equipment are conveyed to the GPCR reactor for destruction

# Gas-Phase Chemical Reduction – Eco Logic Process

## Thermal Reduction Batch Processor (TRBP)



- Accommodates bulk solids such as electrical equipment, drummed material, concrete, wood pallets, etc.
- Desorbs organics from solids:
  - material is loaded in
  - oxygen is purged from vessel
  - heated in presence of hydrogen to appx. 600 °C
- One full-scale TRBP treats up to 75 tonnes per month (can be doubled to 150 tonnes per month with addition of second TRBP)



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<http://>

Full-Scale TRBP at Kwinana, Western Australia



# Destruction and Removal Efficiency (DRE)

## Destruction and Removal Efficiency (DRE)

$$\text{DRE} = 100 \times [1 - (\text{total amount of pollutants in stack emissions}) \div (\text{total amount of pollutants entering a reactor})]$$

- DRE ignores pollutants released as solid or liquid residues (e.g. bottom ash, waste water)

## Destruction Efficiency (DE)

$$\text{DE} = 100 \times [1 - (\text{total amount of pollutants in all outlets}) \div (\text{total amount of pollutants entering a reactor})]$$

# Efficiency of Eco Logic GPCR Technology

## Waste Disposal at General Motors of Canada Ltd.

- ↪ Demonstration project conducted from February 1996 to September 1997, under Ontario Ministry of Environment permits
- ↪ Processed more than 1 000 tons of PCB-contaminated material
- ↪ Waste matrices included electrical equipment, high-strength oil, soil/sediment, concrete, PPE and miscellaneous other solids
- ↪ Extensive regulatory testing showed compliance with all permit requirements, and PCB destruction efficiencies of at least 99.999999% (“8-nines”)

### Commercial-Scale Treatment of PCB Oil containing PCBs, chlorobenzenes and PCDD/F

<i>Regulatory Test</i>	<i>PCBs</i>	<i>CBs</i>	<i>PCDDs/Fs</i>
<i>Destruction and Removal Efficiency DRE (%)</i>			
Test 1	99.9999996	99.9999842	99.999 to 99.9999*
Test 2	99.9999985	99.9999985	
Test 3	99.9999997	99.9999977	
<i>Destruction Efficiency DE (%)</i>			
Test 1	99.9999996	99.9999836	99.999 to 99.9999*
Test 2	99.9999985	99.9999972	
Test 3	99.9999808	99.9999971	

\* Detection limits used in calculation – therefore DREs/Des may be even higher

# Plasma related technology

- ⇒ Plasma technology can be used to convert many complex organic compounds into simpler, harmless molecules such as carbon dioxide, water and hydrogen chloride.
- ⇒ The principle is to subject a stream of the material to be treated to a high-energy electrical discharge.
- ⇒ Extremely high temperatures can be attained in the plasma arc. At such temperatures, chemical substances are rapidly dissociated.

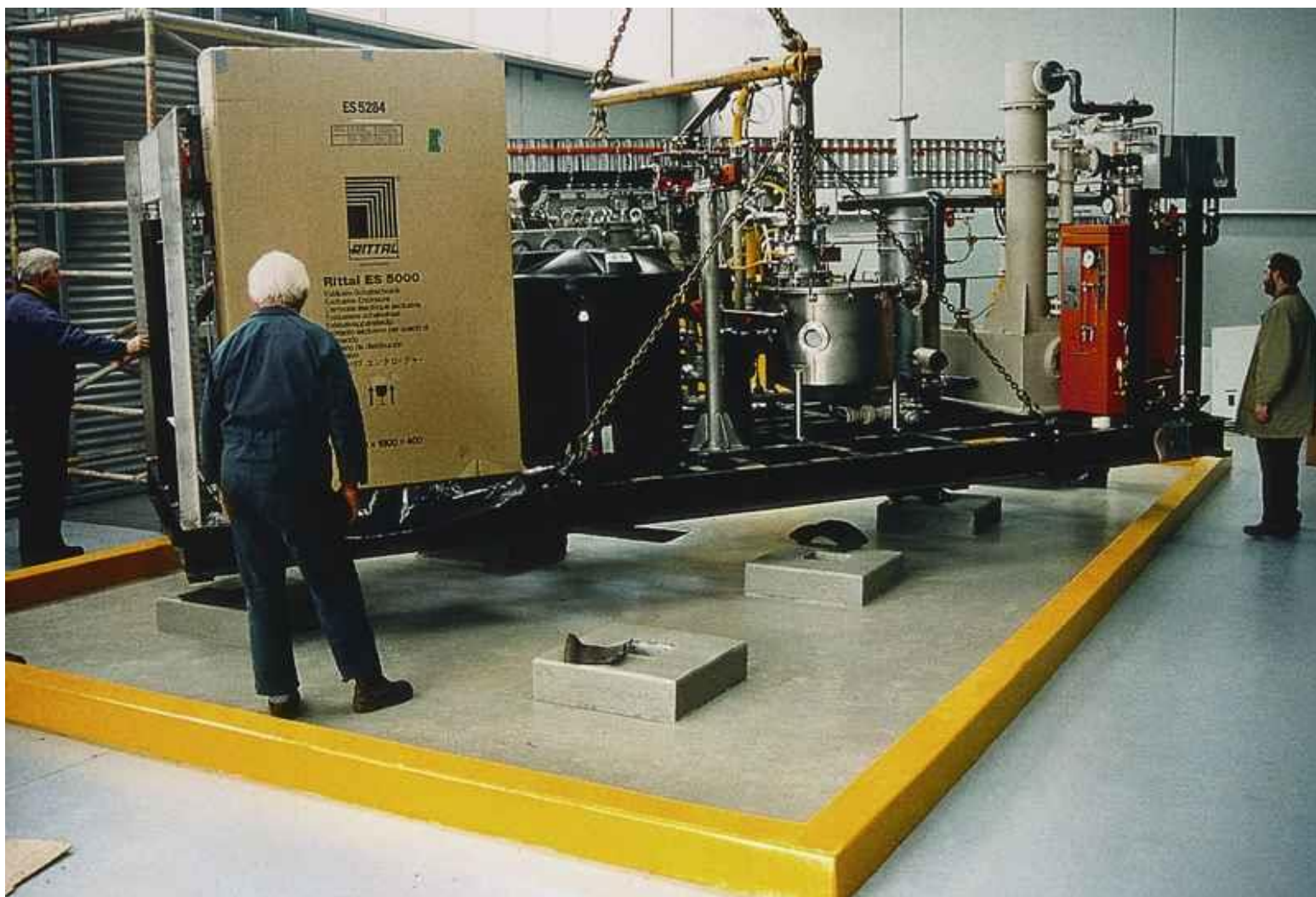
# Plascon - Nufarm Unit



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# Plascon - Skid installation



# Plascon - ODS Unit



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# Plascon - BCDT Unit

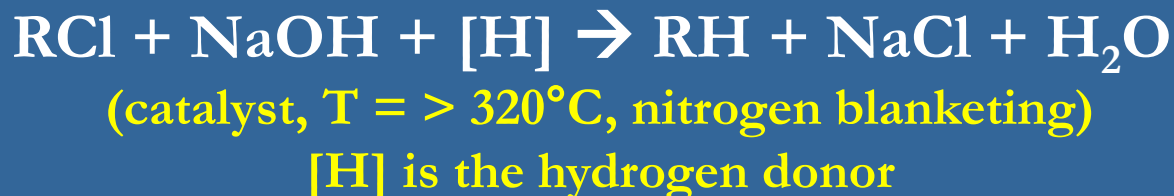


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# Base Catalyzed Dechlorination

- ↪ **Non-conventional heterogeneous catalytic hydrogenation process** which reacts organochlorines with an alkali metal hydroxide or bicarbonate, a hydrogen donor and a proprietary catalyst to produce salts, water and carbonaceous residue.
- ↪ **High destruction efficiencies** have been demonstrated for DDT, PCBs and dioxins/furans in treatability trials.
- ↪ **Limited to approximately 15-30 % strength PCBs.**





# BCD - Enterra plant



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# BCD - Enterra plant



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# Technologies used in the project - BCD

In **BCD**, chemical decomposition of **Cl-HC** takes place. This material is frequently very stable and occurs either as a pure waste or as a concentrated collected in **ITD**.

**BCD** reaction products are salt, water, and residual carbon.

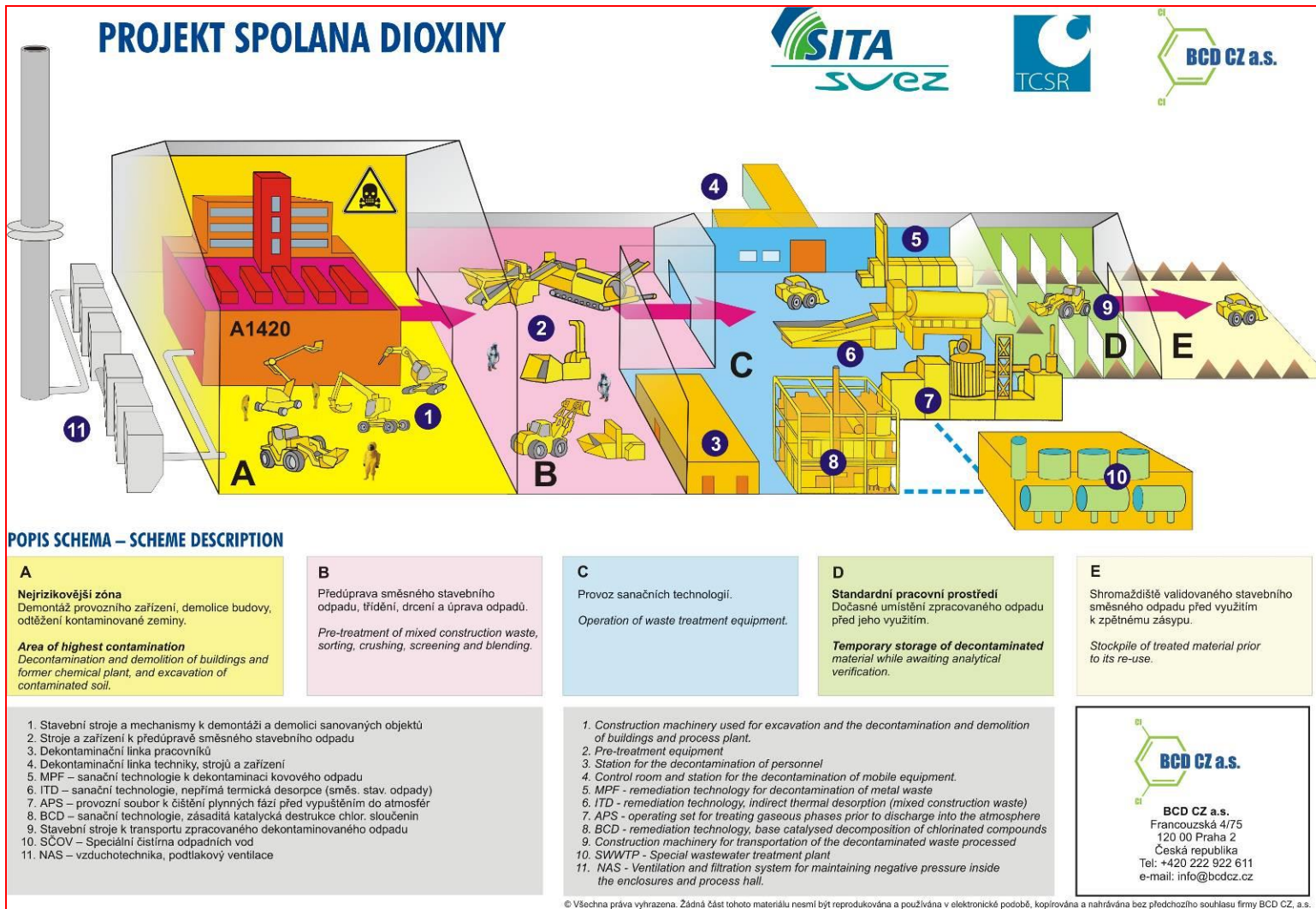
**Metal wastes** were treated in metal parts furnaces.

Cost of the project - 100 mil. EUR

Paid by the CZ Government



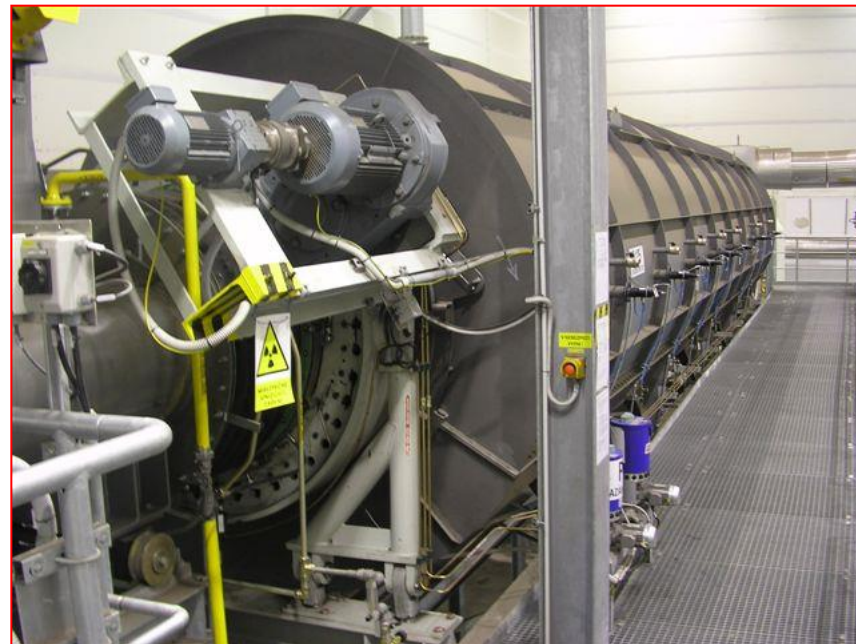
# Project Spolana Neratovice



# MPF Unit



# ITD Unit



# APS Unit



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# BCD Unit



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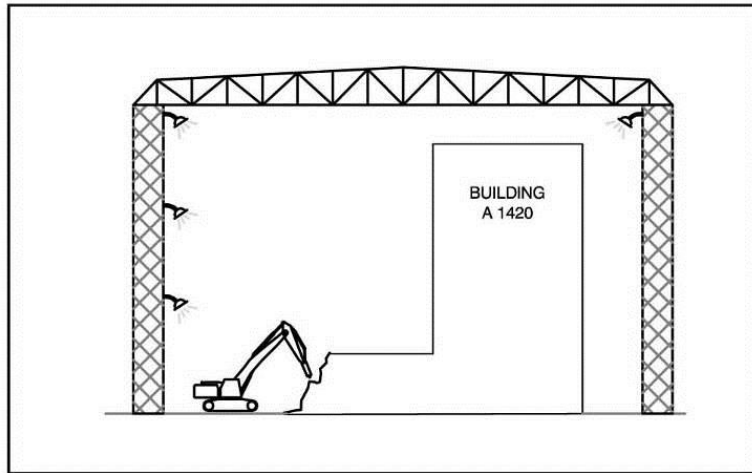
# Content of building – operational equipments



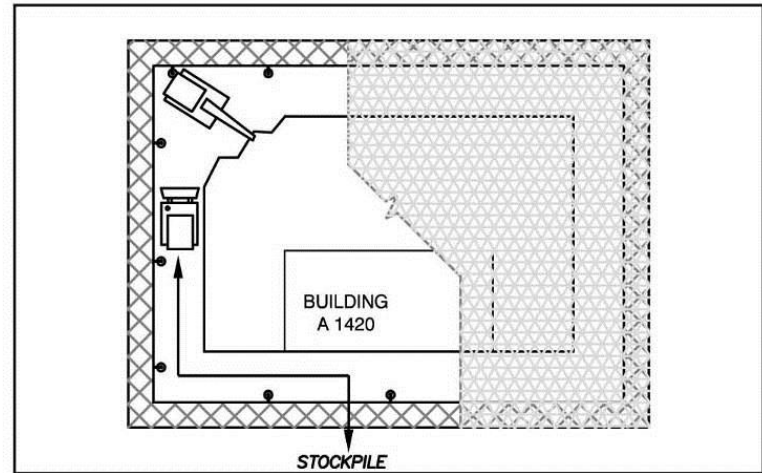
# Contents of building – chemical waste



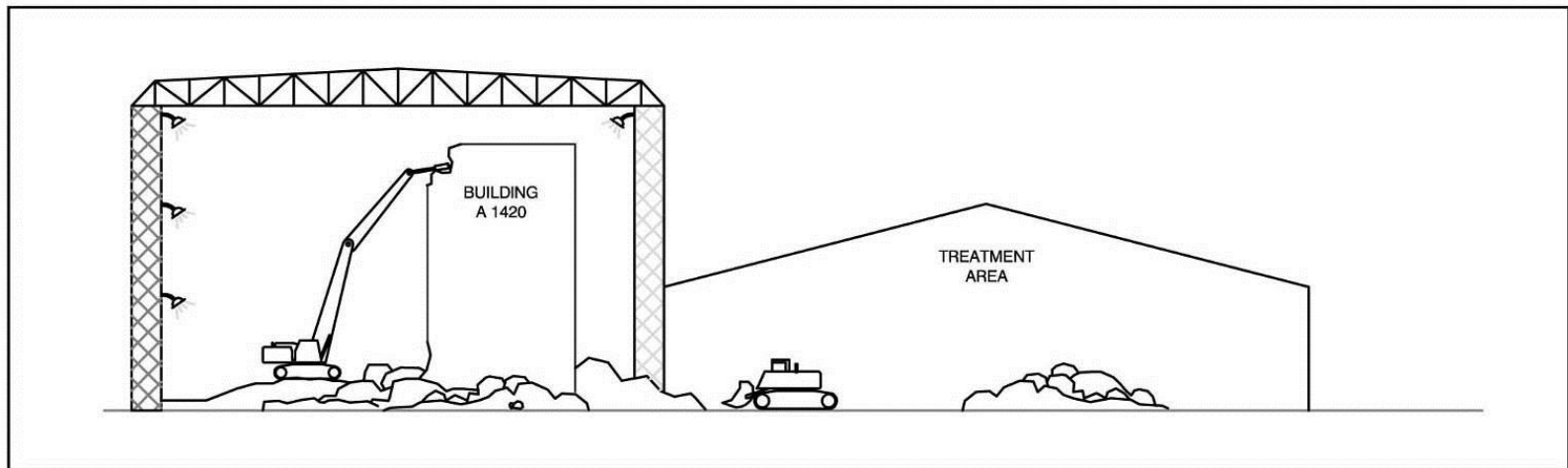
# Demolition of Buildings



SECTION



PLAN



SECTION

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# Sodium reduction

- ↪ Reduction of PCBs with dispersed metallic sodium in mineral oil.
- ↪ Products of the process include non-halogenated polybiphenyl, sodium chloride, petroleum based oils and water (pH > 12).
- ↪ Has been used widely for in-situ removal of PCBs from active transformers.
- ↪ Has been used widely for in-situ removal of PCBs from active transformers.

# Solvated electron technology

- ↪ Solvated electron solutions are produced by dissolving sodium metal in anhydrous ammonia at room temperature. The solvated electrons reduce POPs wastes metal salts and simple hydrocarbon compounds. eg. PCBs are reduced to petroleum hydrocarbons, sodium chloride, and sodium amide. Materials with a high water content must be de-watered prior to treatment.
- ↪ High destruction efficiencies have been reported for DDT, dioxins/furans and PCBs.

# PCB waste disposal

- ↪ **The ideal disposal operation does not exist.**
- ↪ **The method which is used depends** on the type of waste, on the waste produced by the disposal operation, on the technical possibilities, on the economical conditions as well as on the experience and the knowledge of the administration and the public.
- ↪ However in every case the wastes should be disposed of in an environmentally sound manner, that is, **using the best available techniques and the best environmental practices**, taking into account the whole environmental impact of the operations.

# High-temperature incineration

- ↪ **The great majority of PCB wastes being destroyed today are being destroyed by incineration.** The reason for this is that high temperature incineration is a technology which is well developed and readily available in many industrialized countries.
- ↪ **Most of these plants are to found in Europe and America.** They have not necessarily all been built for the purpose of destroying PCBs and halogenated compounds, as some have been built for the in-house wastes of chemical companies.
- ↪ **There are some industrialised countries no longer permit such incinerators,** the most prominent examples being Japan (PCBs) and Australia; these countries must of necessity find alternative destruction technologies for their PCB-containing materials.

Liquid Waste  
Tank Farm

Solid and Sludge  
Waste Bunker

Heat Recovery  
Steam Boiler

Electrostatic  
Precipitator for  
Fly Ash Removal

Baghouse  
Adsorber for  
POPs Removal

SCR System  
for NO<sub>x</sub> and  
POPs  
Removal

Solid Hazardous  
Waste Delivery (Bulk  
and Drums)

Rotary Kiln  
and  
Afterburning  
Chamber

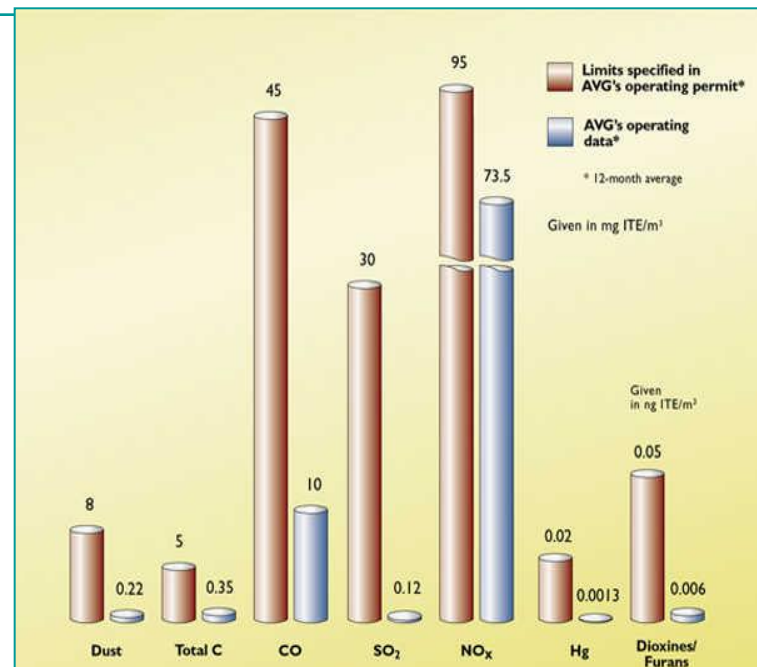
Spray Dryer for  
Wastewater  
Evaporation

Wet Scrubbers for  
Acid Gas Removal

Recuperative Heat  
Exchanger for  
Flue Gas Reheat

## POPs Destruction Performance of Rotary Kiln Type Incinerators depends on:

- ↪ Rotary kiln combustion temperature  $\geq 1\ 000\ ^\circ\text{C}$
- ↪ Secondary combustion chamber temperature  $\geq 1\ 200\ ^\circ\text{C}$
- ↪ O<sub>2</sub>-content  $\geq 6\ \%\text{vol.}$  (typically  $\sim 10\ \%\text{vol.}$ )
- ↪ Multi-stage flue gas cleaning system including at least one highly effective dedicated POPs removal stage
- ↪ As designed operation and maintenance at all times



## Performance of Incineration Technologies



# High-temperature incineration

The incineration of waste is a method available on an industrial scale, and for which comprehensive knowledge and data are available, by which the harmfulness of a large number of substances can be greatly reduced.

The following goals are being pursued by means of incineration:

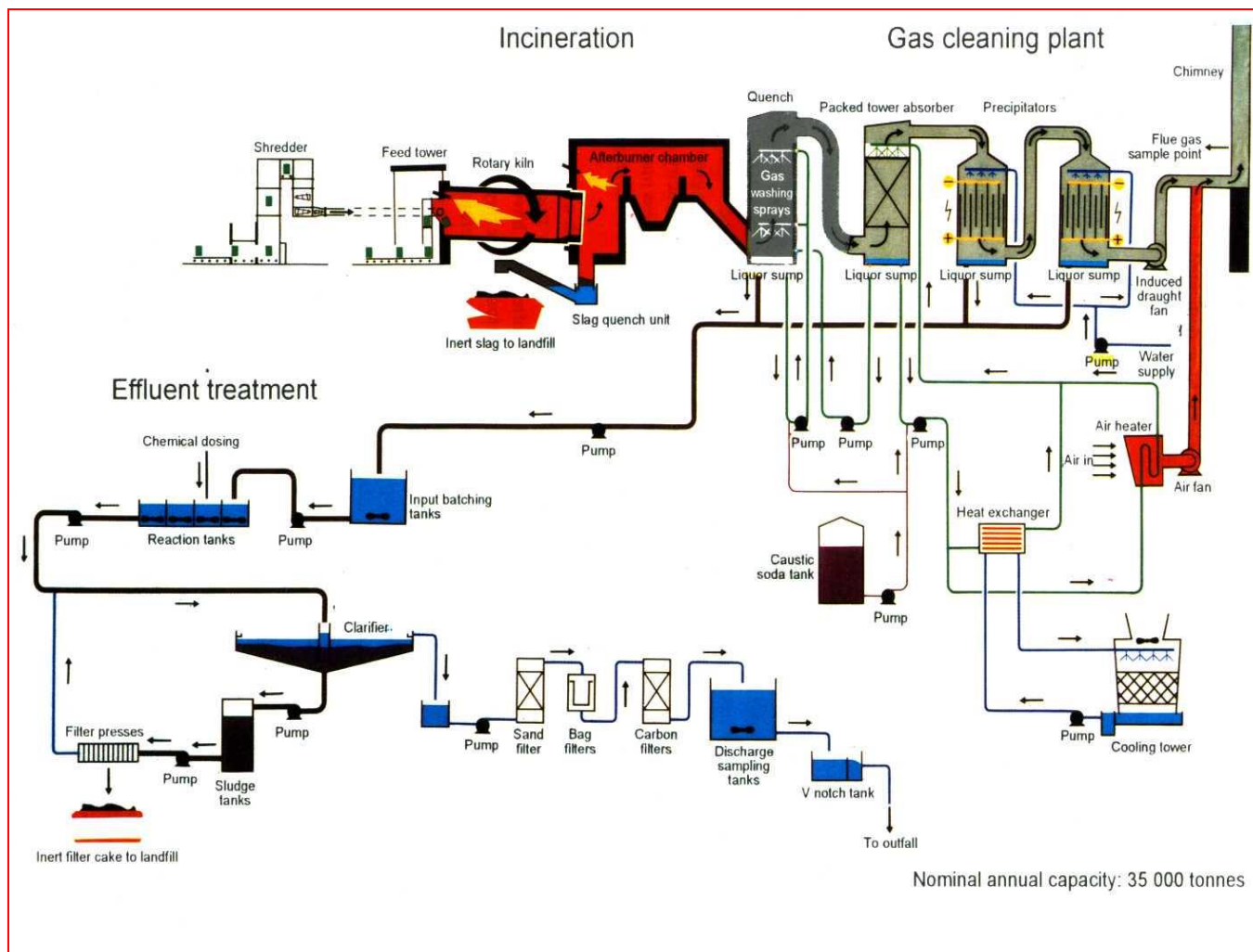
- ↪ the disposal of solid, liquid, and semi fluid wastes which cannot be landfilled or treated chemically or physically without harm to the environment, because of their composition and content of decomposable substances,
- ↪ minimisation of the hazard potential and content of harmful substances of the wastes, especially by breaking down organic compounds,
- ↪ substantial reductions in volume and weight,
- ↪ utilisation of the energy released.

# Technology description

High temperature hazardous waste incinerators are available in a number of configurations and principles.

Typically a process for treatment involves heating to a temperature higher than 850 °C or, if the chlorine content is above 1 %, greater than 1100 °C, with a residence time greater than 2 seconds, under conditions that assure appropriate mixing and subsequent destruction.

# Dedicated hazardous waste incinerator



# Temperature and residence time

Combustion temperature and residence time needed for mixed hazardous wastes cannot be readily calculated and are often determined empirically.

Some common solvents such as alcohols and toluene can easily be combusted at temperatures less than 1 000 °C and less than one second residence time, while other more complex organic halogens require more stringent conditions.

# Regulations

## US EPA Toxic Substances Control Act (TSCA) PCBs Incineration Criteria

“...more complex organic halogens such as PCB requires 1 200 °C and 2 seconds residence time ”

A DRE of 99.9999% is required by TSCA for the incineration of PCBs

## EU Directive 2000/76/EC on Incineration of Waste regulates Co-incineration of Hazardous Waste in Cement Kilns

“...if more than 1 % of halogenated organic substances, expressed as chlorine, are incinerated, the temperature has to be raised to minimum 1 100 °C during at least two seconds”.

# Technology description

**Hazardous waste** is normally incinerated in two types of facilities: merchant plants who accept different types of waste for disposal; and dedicated incinerators that handle a particular waste stream.

**The most common combustion technology** in hazardous waste incineration is the rotary kiln.

Facilities in the merchant sector range in size from 30 000 to 100 000 tons/year throughput.

**Dedicated hazardous waste incinerators** use a variety of incineration, pyrolysis, and plasma treatment techniques.

Similar to the incineration of municipal solid waste, hazardous waste incineration offers the benefits of **volume reduction and energy recovery**.

# Flue gas treatment

## GENERAL

- ↪ Dust separation
- ↪ Scrubbing processes
- ↪ De-SO<sub>x</sub>
- ↪ De-NO<sub>x</sub>
- ↪ Afterburners
- ↪ Catalytic destruction
- ↪ Sorption processes

## DIOXINS/FURANS

- ↪ Afterburners
- ↪ Rapid quench system
- ↪ Dust separation
- ↪ Scrubbing processes
- ↪ Sorption process
- ↪ Catalytic oxidation

# Sound management of unintended POPs by-products

↪ Alternatives

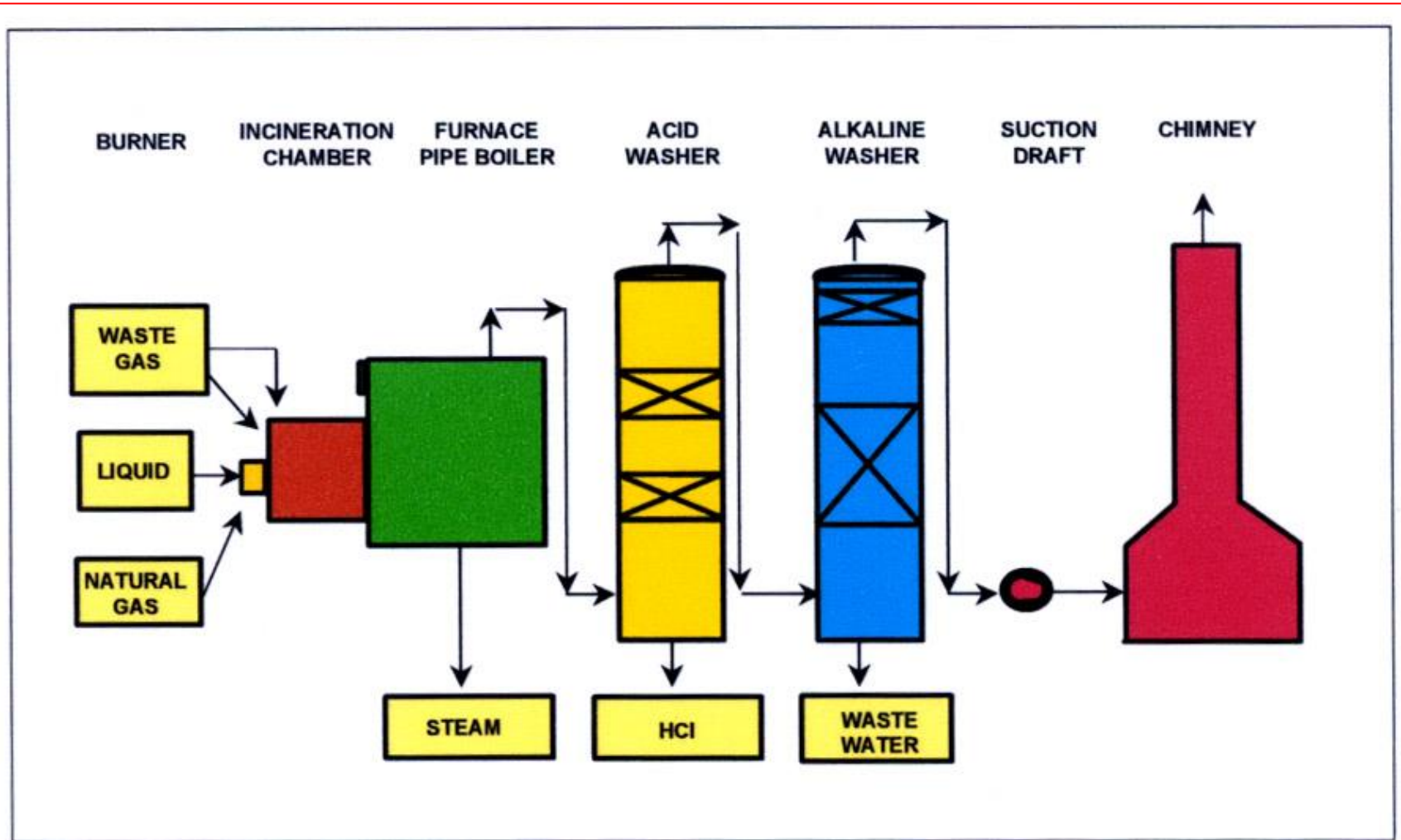
↪ Preventive measures

↪ Secondary measures - control and reduction of releases to:

- ❖ Air
- ❖ Water
- ❖ Land
- ❖ Wastes
- ❖ Products



# Dedicated hazardous waste incinerator for treating liquid and gaseous chlorinated wastes at a chlorinated chemical manufacturing facility



# Dedicated hazardous waste incinerator



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# Dedicated hazardous waste incinerator



# Dedicated hazardous waste incinerator



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# Dedicated hazardous waste incinerator



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# Formation and release of unintentional POPs

**Emission testing** has confirmed that composition of the waste, furnace design, temperatures in the post-combustion zone, and the types of air pollution control devices (APCD) used to remove pollutants from the flue gases are important factors in determining the extent of POPs formation and release.

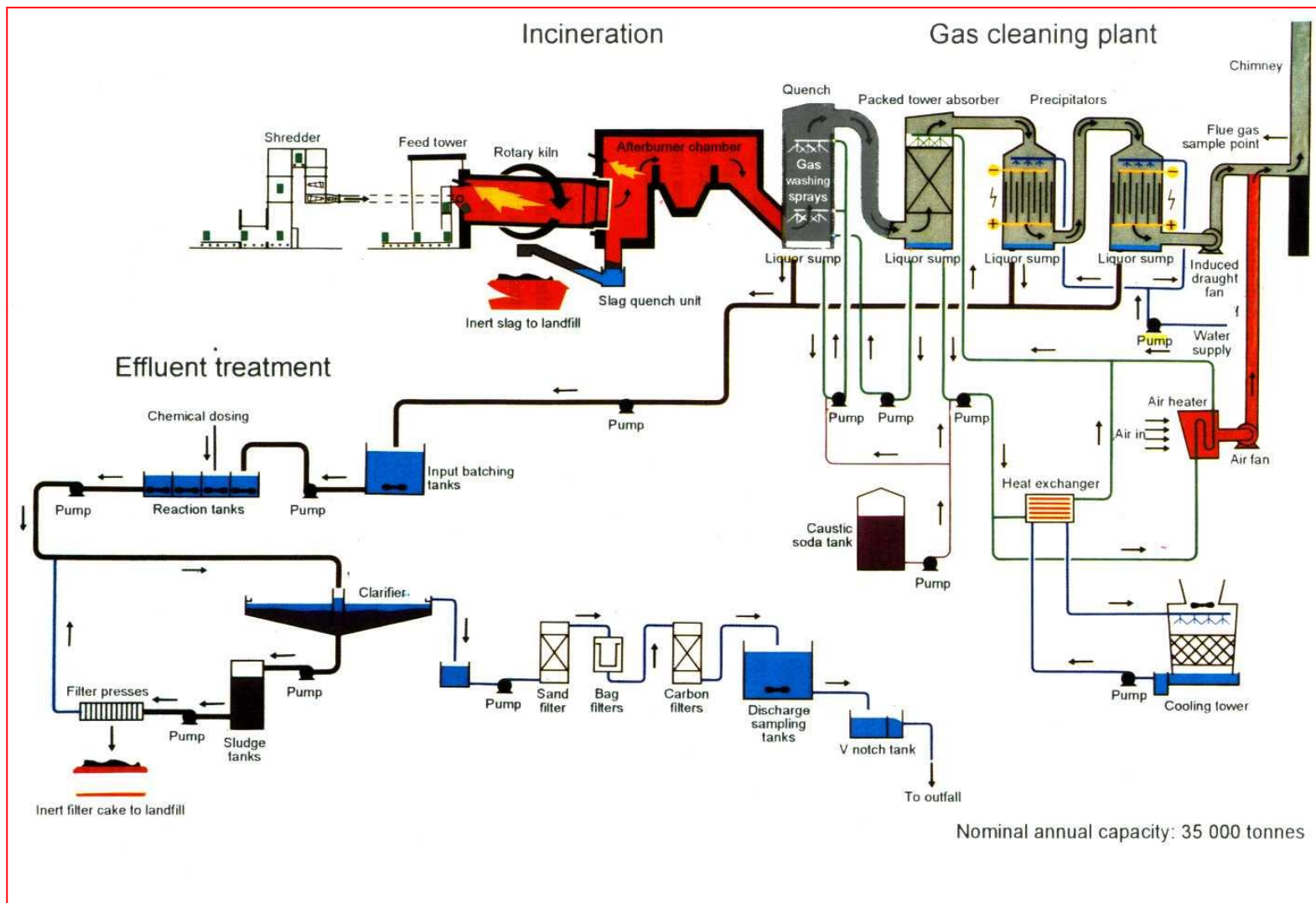
**Depending on the combination of these factors**, POPs releases can vary over several orders of magnitude per ton of waste incinerated.

# Waste incineration

## Municipal, hazardous solid waste and sewage sludge:

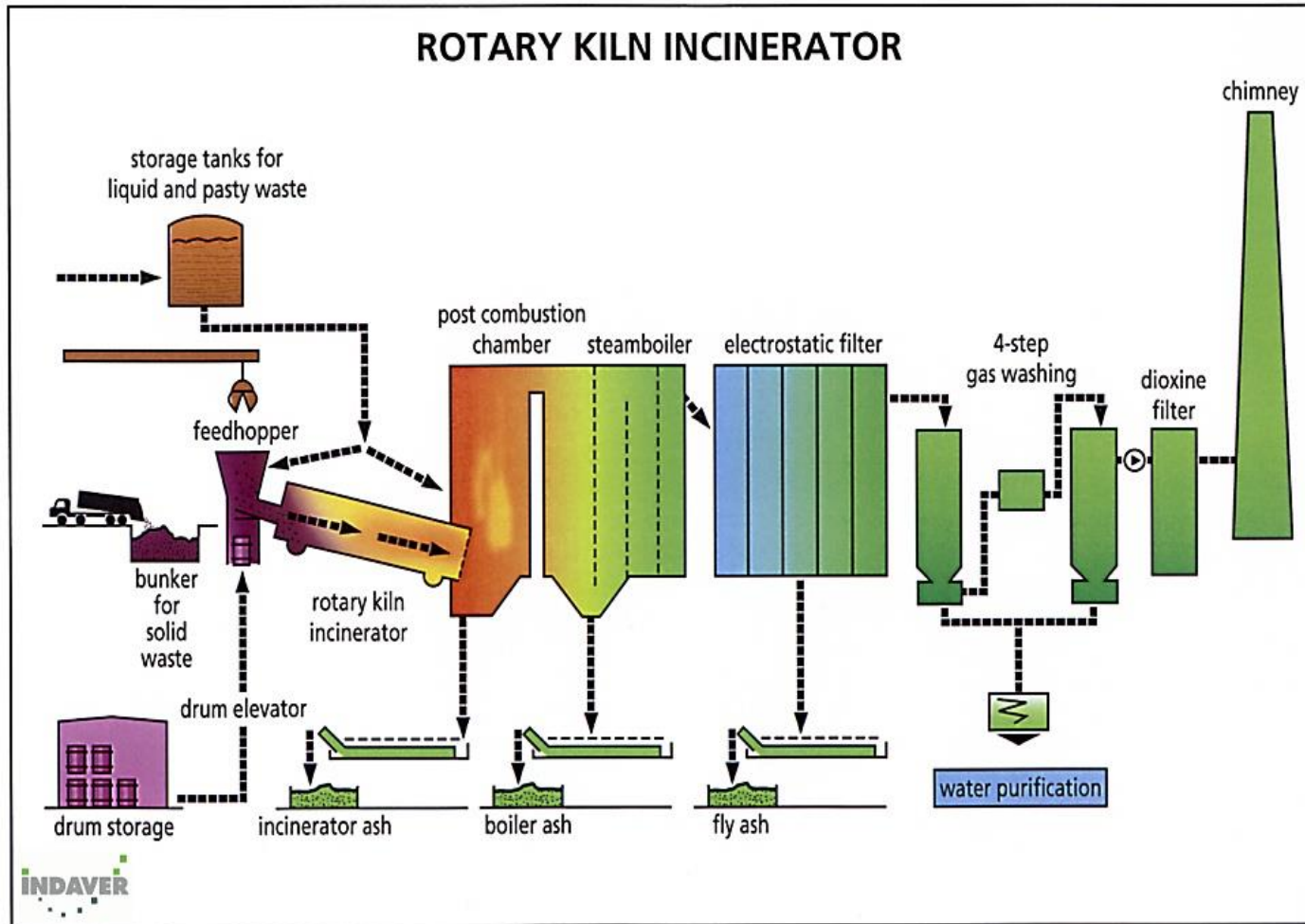
- ↪ **Alternatives:** waste minimization including recovery, reuse, recycling, waste separation and cleaner technologies
- ↪ **Purpose of waste incineration:** volume reduction, energy recovery, destruction and minimization of hazardous constituents, disinfection, reuse of some residues
- ↪ **BAT/BEP/BACT:** prevent or minimize POPs releases, proper waste handling, ensure good combustion, avoid formation conditions, capturing POPs that are formed and handling residues appropriately
- ↪ **Achievable performance levels:** 0.1-0.1 ng TEQ.Nm<sup>-3</sup>

# Hazardous waste incineration plant





# Example of flue gas cleaning technology

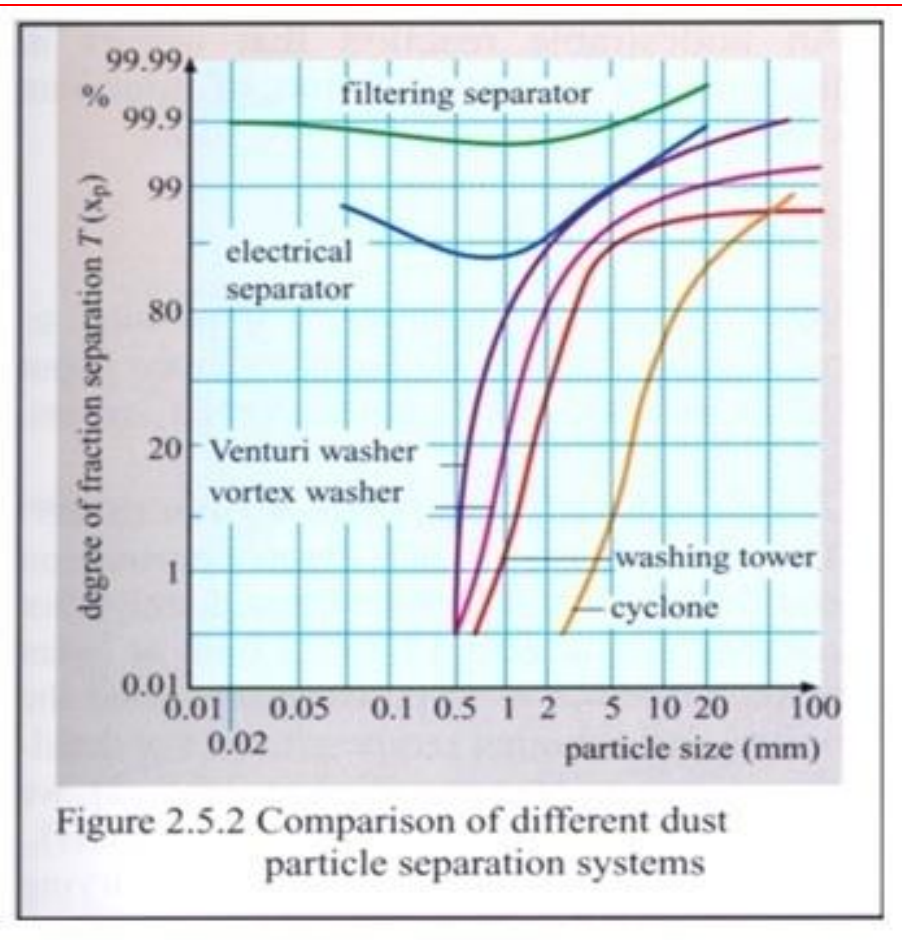


# Examples of APCD's relevant to the prevention or reduction of unintentional POPs releases

- ↪ Cyclones and multi-cyclones
- ↪ Electrostatic precipitators – wet, dry or condensation
- ↪ Fabric filters – including catalytic bag filters
- ↪ Static bed filters
- ↪ Scrubbing systems - wet, spray dry, or ionization
- ↪ Selective catalytic reduction (SCR)
- ↪ Rapid quenching systems
- ↪ Carbon adsorption

# Dust removal

- ↪ Mechanic separation  
wet/dry ( $300 - 150 \text{ mg.m}^{-3}$ )
- ↪ Electrostatic precipitation  
dry/wet ( $5 - 25 \text{ mg.m}^{-3}$ )
- ↪ Textile filters  
mechanic/catalytic  
(less than  $5 \text{ mg.m}^{-3}$ )



# Electrostatic precipitator principle

**Unintentional POPs formation** can occur within the ESP at temperatures in the range of 200 °C to about 450 °C.

Operating the ESP within this temperature range can lead to the formation of unintentional POPs in the combustion gases released from the stack.

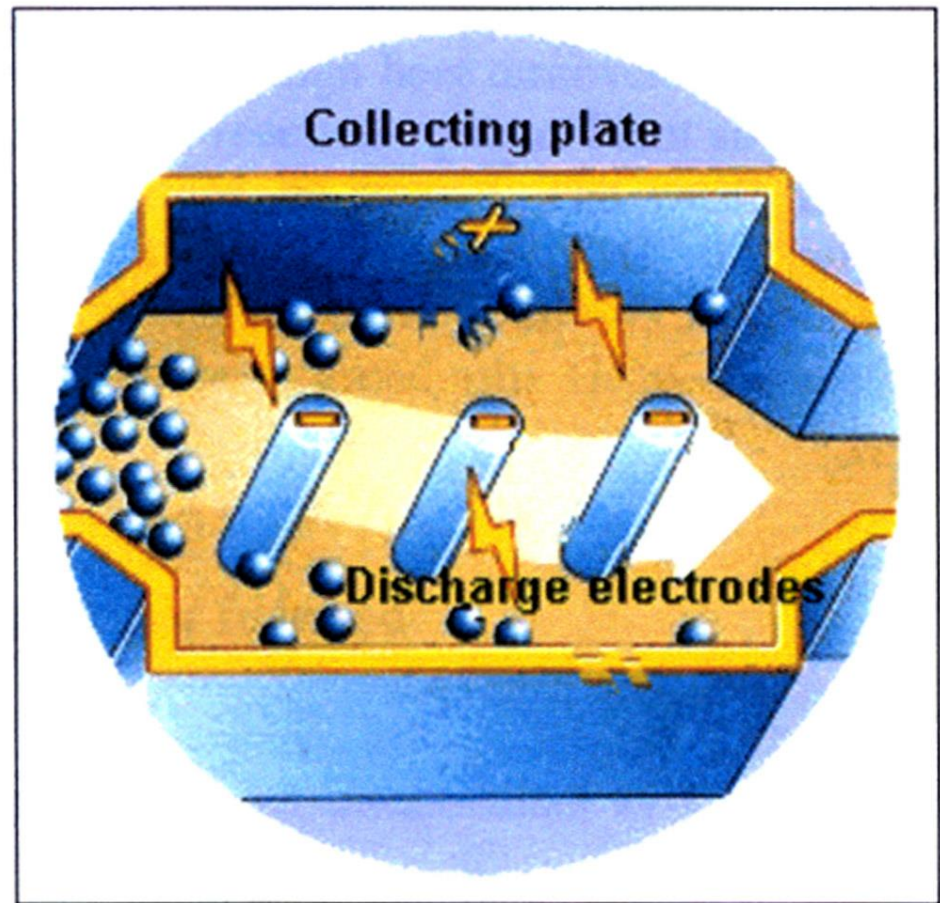


Figure 4.1 Electrostatic Precipitator Principle [source: EU BREF, 2004]

# Best Environmental Practices for Waste Incineration

Well-maintained facilities, well-trained operators, a well-informed public, and constant attention to the process are all important factors in minimizing the formation and release of the unintentional POPs from the incineration of waste.

In addition, **effective waste management strategies** (e.g., waste minimization, source separation, and recycling), by altering the volume and character of the incoming waste, can also significantly impact releases.

# Waste Inspection and Characterization

Waste type	Techniques	Comments
<b>Mixed municipal wastes</b>	<ul style="list-style-type: none"> <li>• visual inspection in bunker</li> <li>• spot checking of individual deliveries by separate off loading</li> <li>• weighing the waste as delivered</li> <li>• radioactive detection</li> </ul>	Industrial and commercial loads may have elevated risks
<b>Pre-treated municipal wastes and RDF</b>	<ul style="list-style-type: none"> <li>• visual inspection</li> <li>• periodic sampling and analysis for key properties/substances</li> </ul>	
<b>Hazardous wastes</b>	<ul style="list-style-type: none"> <li>• visual inspection</li> <li>• sampling/analysis of all bulk tankers</li> <li>• random checking of drummed loads</li> <li>• unpacking and checking of packaged loads</li> <li>• assessment of combustion parameters</li> <li>• blending tests on liquid wastes prior to storage</li> <li>• control of flash-point for wastes in the bunker</li> <li>• screening of waste input for elemental composition e.g. by EDXRF</li> </ul>	<p>Extensive and effective procedures are particularly important for this sector.</p> <p>Plants receiving mono-streams may be able to adopt more simplified procedures</p>
<b>Sewage sludges</b>	<ul style="list-style-type: none"> <li>• periodic sampling and analysis for key properties and substances</li> <li>• checking for stones/metal prior to drying stages</li> <li>• process control to adapt to sludge variation</li> </ul>	

# Proper Handling, Storage, and Pre-Treatment

**Storage areas** must be properly sealed with controlled drainage and weatherproofing.

**Fire detection and control systems** for these areas should be considered.

**Storage and handling areas** should be designed to prevent contamination of environmental media and to facilitate clean up in the event of spills or leakage.

**Odors** can be minimized by using bunker air for the combustion process.

# Proper Handling, Storage, and Pre-Treatment

Waste type	Segregation techniques
<b>Mixed municipal wastes</b>	<ul style="list-style-type: none"><li>• segregation is not routinely applied unless various distinct waste streams are received when these can be mixed in the bunker</li><li>• bulky items requiring pretreatment can be segregated</li><li>• emergency segregation areas for rejected waste</li></ul>
<b>Pre-treated municipal wastes and RDF</b>	<p>segregation not routinely applied</p> <ul style="list-style-type: none"><li>• emergency segregation areas for rejected waste</li></ul>
<b>Hazardous wastes</b>	<ul style="list-style-type: none"><li>• extensive procedures required to separate chemically incompatible materials (examples given as follows)</li><li>• water from phosphides</li><li>• water from isocyanates</li><li>• water from alkaline metals</li><li>• cyanide from acids</li><li>• flammable materials from oxidising agents</li><li>• maintain separation of pre-segregated packaged delivered wastes</li></ul>
<b>Sewage sludges</b>	<ul style="list-style-type: none"><li>• wastes generally well mixed before delivery to plant</li><li>• some industrial streams may be separately delivered and require segregation for blending</li></ul>



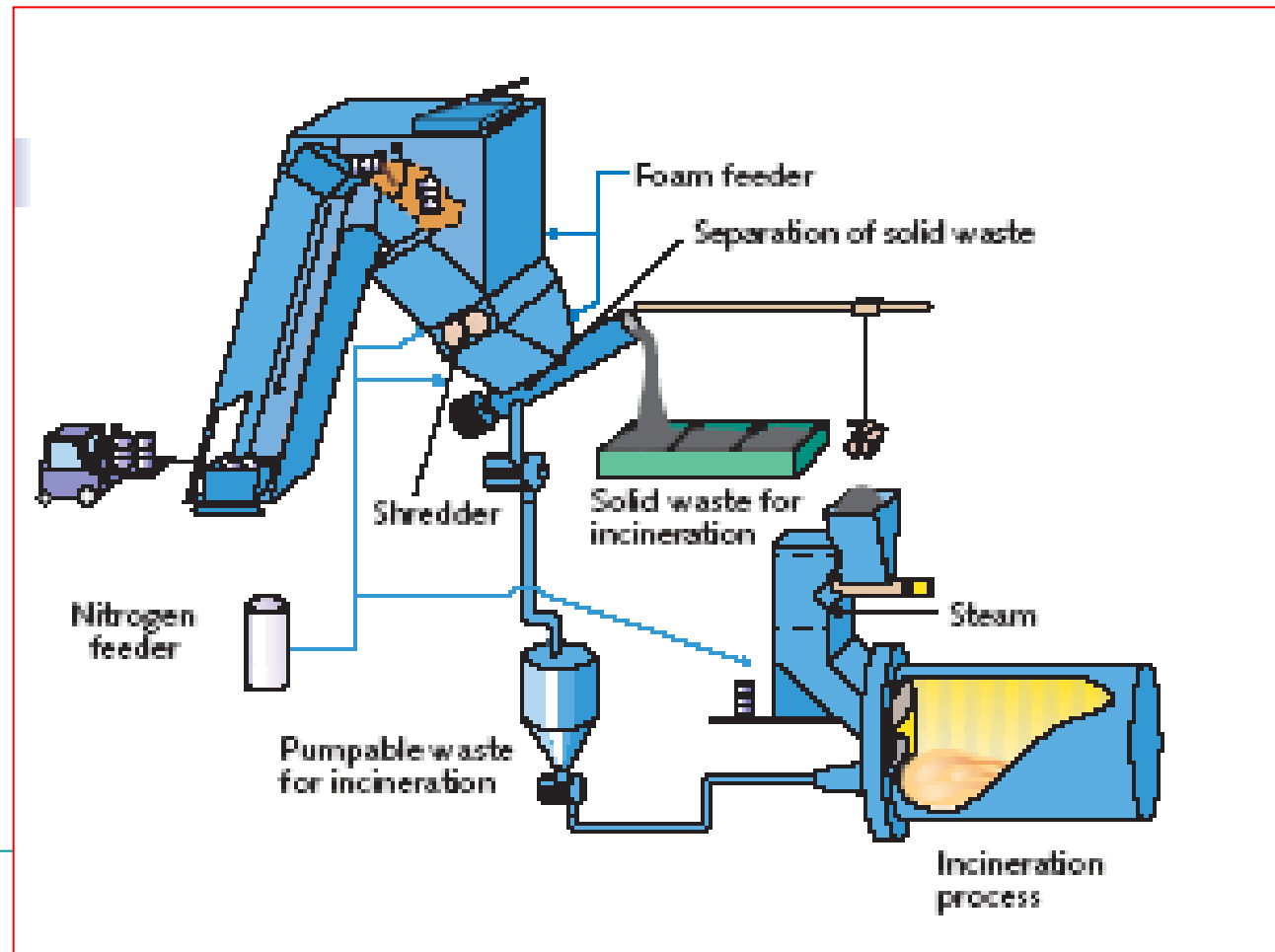
# Minimizing Storage Times

**Minimizing the storage period** will help prevent putrefaction and unwanted reactions, as well as the deterioration of containers and labeling.

Managing deliveries and communicating with suppliers will help ensure that reasonable storage times are not exceeded.

# Establishing Quality Requirements for Waste Fed

Facilities must be able to accurately predict the heating value and other attributes of the waste being combusted in order to ensure that the design parameters of the incinerator are being met.

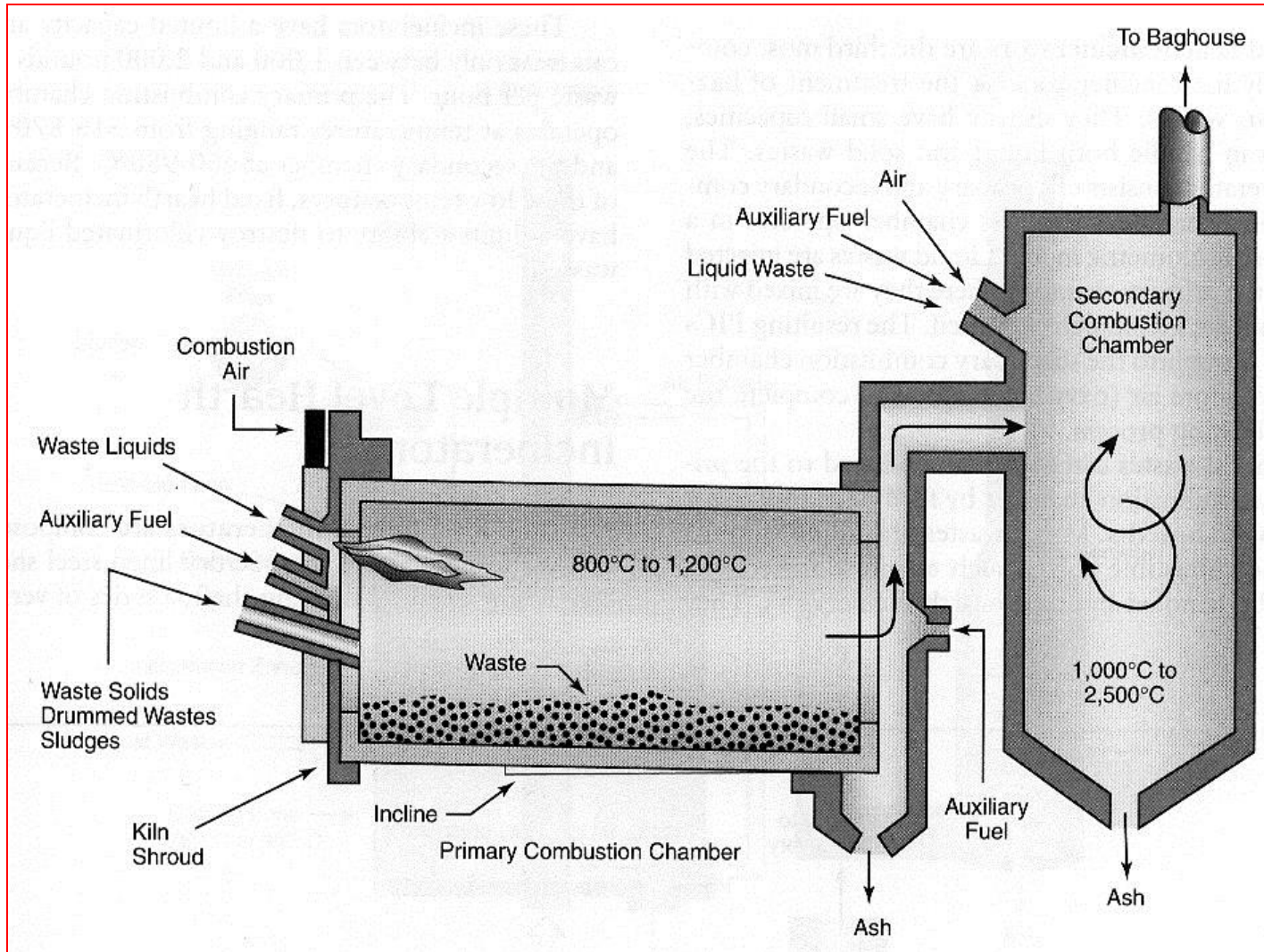


# Monitoring

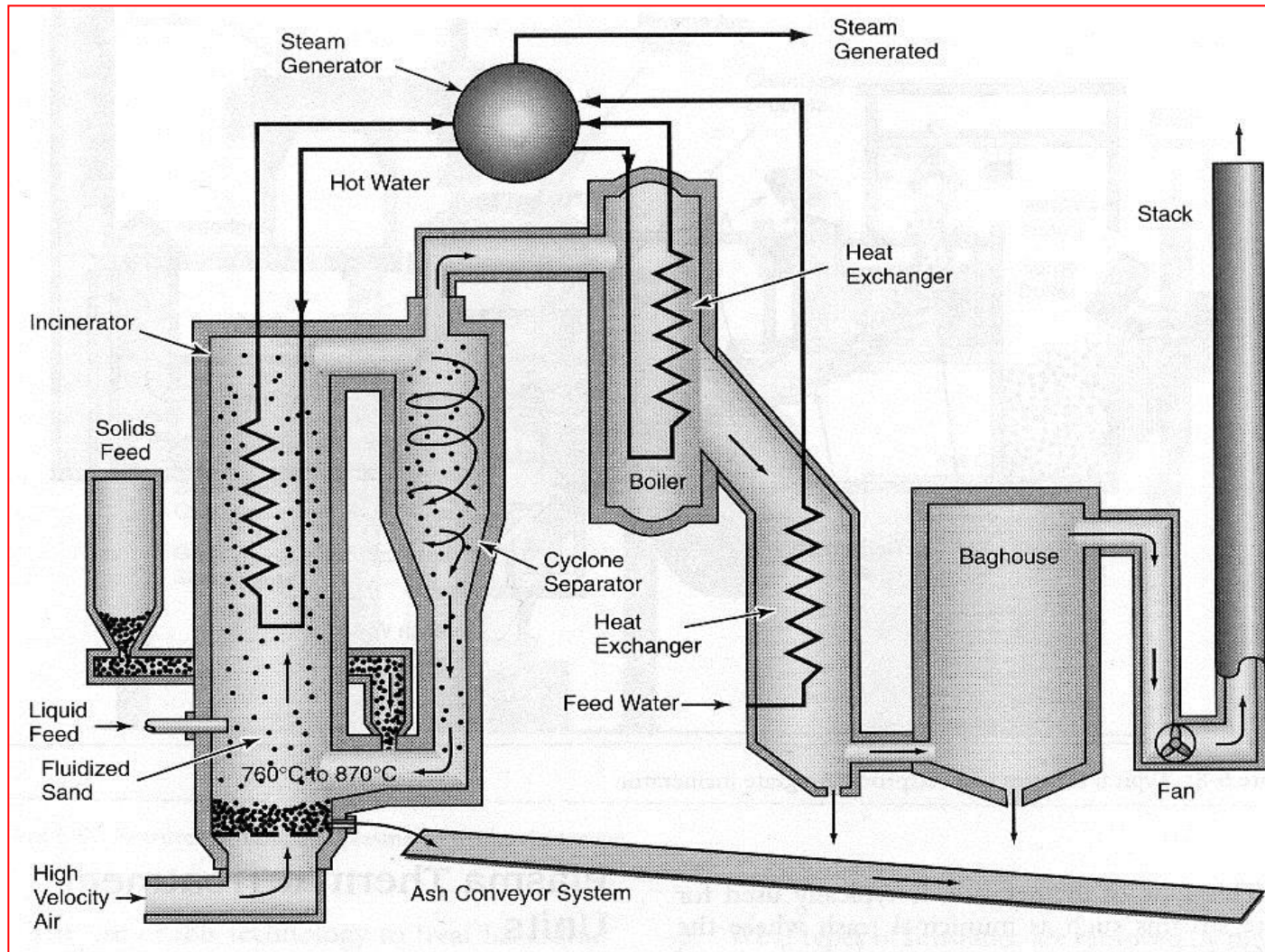
In addition to carbon monoxide, oxygen and  $\text{NO}_x$  in the flue gas, air flows and temperatures, pressure drops, and pH in the flue gas **can be routinely monitored at reasonable cost.**

**While these measurements in some instances can represent reasonably good surrogates for the potential for unintentional POPs formation and release, periodic measurement of PCDDs/Fs in the flue gas will aid in ensuring that releases are minimized and the incinerator is operating properly.**

# Rotary kiln incinerator



# Circulating fluidised bed

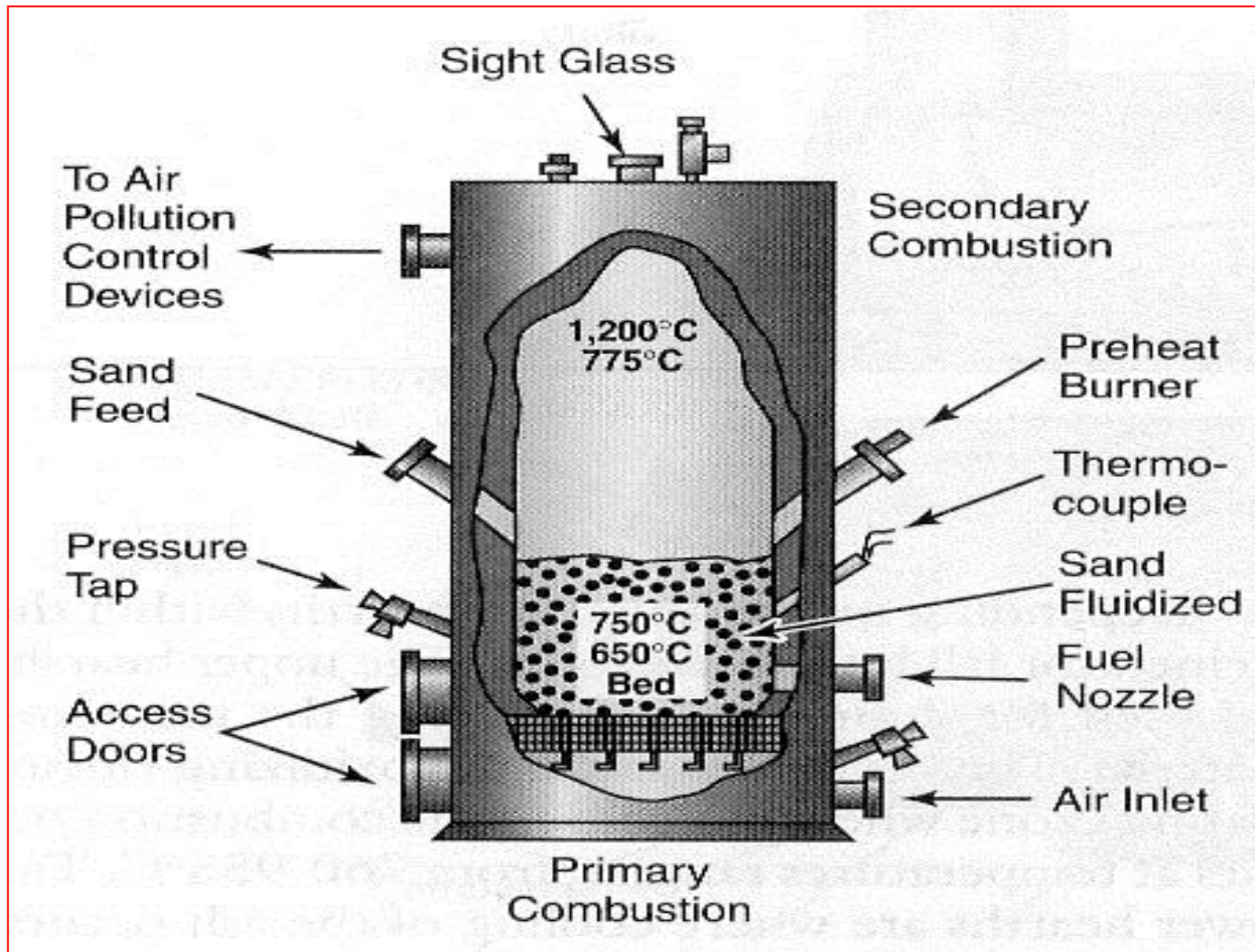


# Maintaining Public Awareness and Communication

Successful incineration projects have been characterized by:

- ↪ holding regular meetings with concerned citizens;
- ↪ providing days for public visitation;
- ↪ posting release and operational data to the Internet; and
- ↪ displaying real time data on operations and releases at the facility site.

# Bubbling fluidised bed



# BAT - General Combustion Techniques

- ↪ Ensure design of furnace is appropriately matched to characteristics of the waste to be processed.
- ↪ Maintain temperatures in the gas phase combustion zones in the optimal range for completing oxidation of the waste.
- ↪ Provide for sufficient residence time (e.g. 2 seconds) and turbulent mixing in the combustion chamber(s) to complete incineration.
- ↪ Pre-heat primary and secondary air to assist combustion.
- ↪ Use continuous rather than batch processing wherever possible to minimize start-up and shut-down releases.



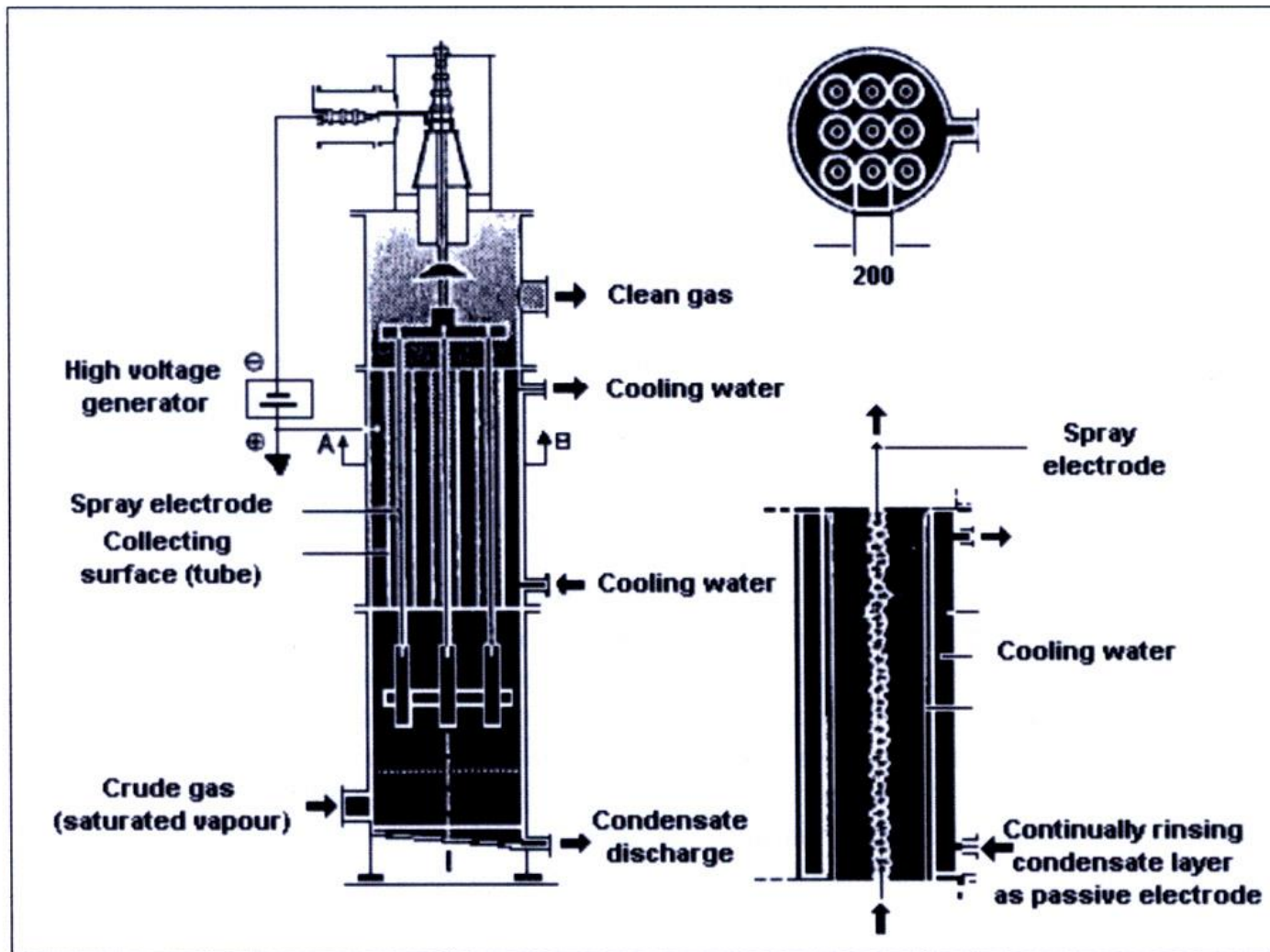
# BAT - General Combustion Techniques

- ↪ Establish systems to **monitor critical combustion parameters** including grate speed and temperature, pressure drop, and levels of CO, CO<sub>2</sub>, O<sub>2</sub>.
- ↪ Provide for **control interventions to adjust waste feed, grate speed, and temperature, volume, and distribution of primary and secondary air.**
- ↪ Install **automatic auxiliary burners** to maintain optimal temperatures in the combustion chamber(s).

# BAT – Hazardous Waste Combustion Techniques

- ↪ **Rotary kilns** are well demonstrated for the incineration of hazardous waste and can accept liquids and pastes as well as solids.
- ↪ **Water-cooled kilns** can be operated at higher temperatures and allow acceptance of wastes with higher energy values.
- ↪ **Waste consistency (and combustion)** can be improved by shredding drums and other packaged hazardous wastes.
- ↪ **A feed equalization system** e.g., screw conveyors that can crush and provide a constant amount of solid hazardous waste to the furnace, will ensure smooth feeding.

# Condensation electrostatic precipitator



# BAT – Flue Gas Treatment

The type and order of treatment processes applied to the flue gases once they leave the incineration chamber is important, both for optimal operation of the devices as well as for the overall cost effectiveness of the installation.

Waste incineration parameters that affect the selection of techniques include:

- ↪ waste type - composition and variability;
- ↪ type of combustion process;
- ↪ flue gas flow and temperature;
- ↪ and the need for, and availability of, wastewater treatment.

# Fabric filters

**Fabric filters** are also referred to as baghouses or dust filters.

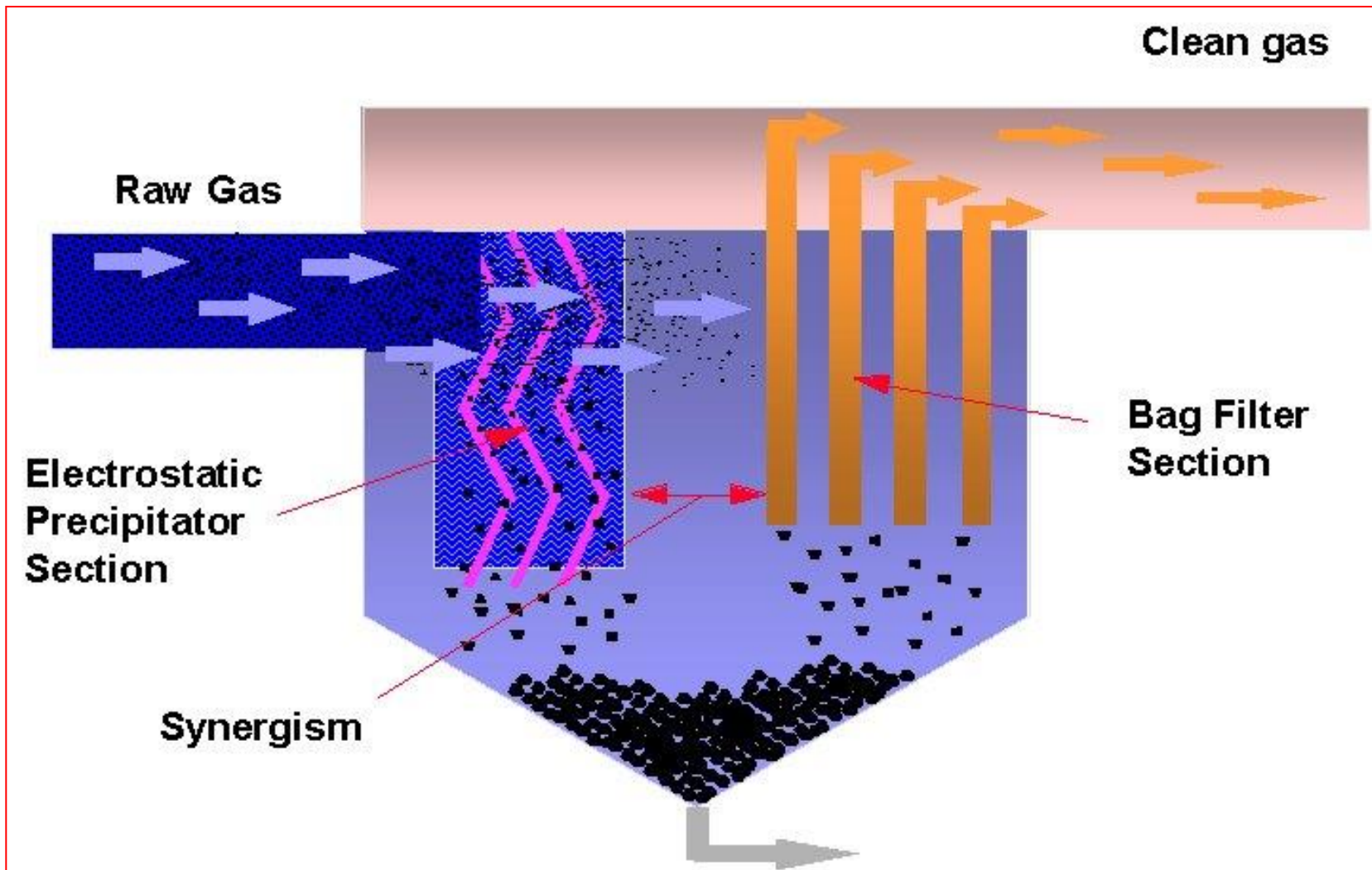
These **particulate matter control devices** can effectively remove unintentional POPs that may be associated with particles and any vapors that adsorb to the particles in the exhaust gas stream.

**Filters** are usually 16 to 20 cm diameter bags, 10 m long, made from woven fiberglass material, and arranged in series.

**Fabric filters** are sensitive to acids; therefore, they are usually operated in combination with spray dryer adsorption systems for upstream removal of acid gases.



# Combined dust removal



# Desulphurization process

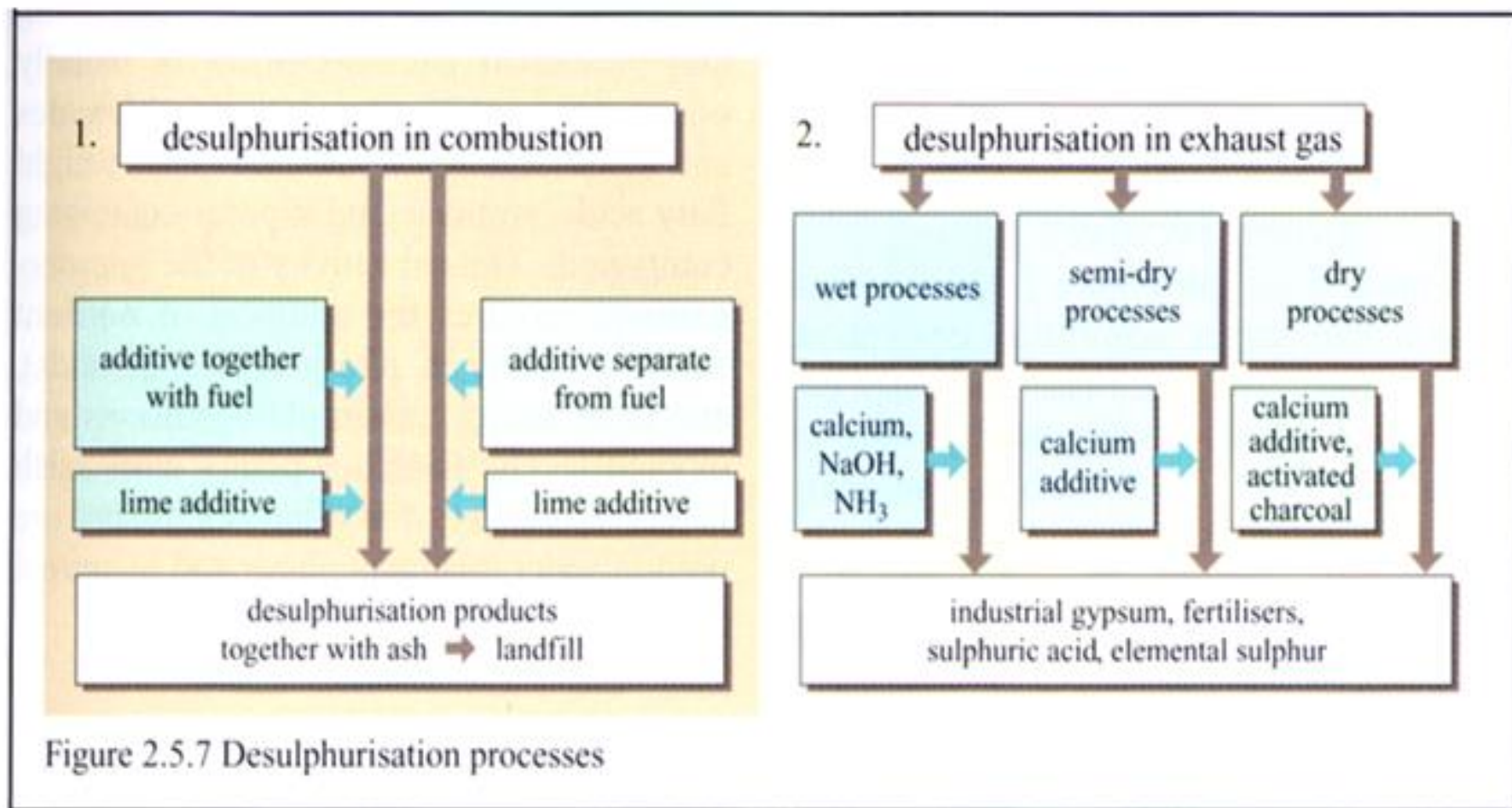


Figure 2.5.7 Desulphurisation processes

# De-NO<sub>x</sub>

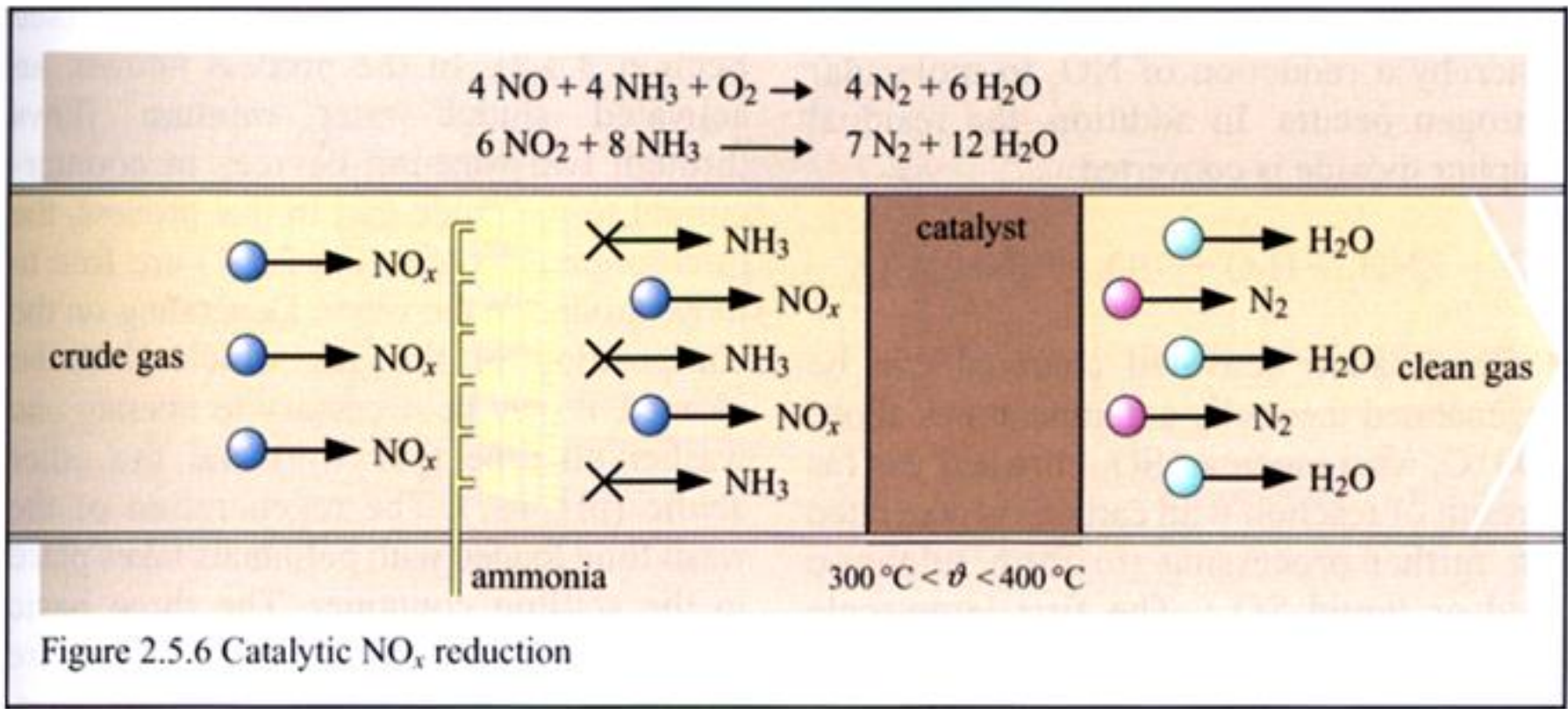
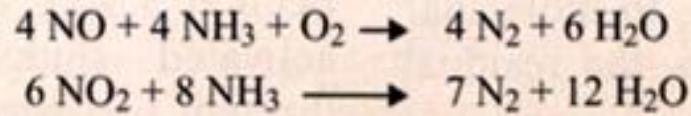


Figure 2.5.6 Catalytic NO<sub>x</sub> reduction



# De-SO<sub>x</sub> and De-NO<sub>x</sub>

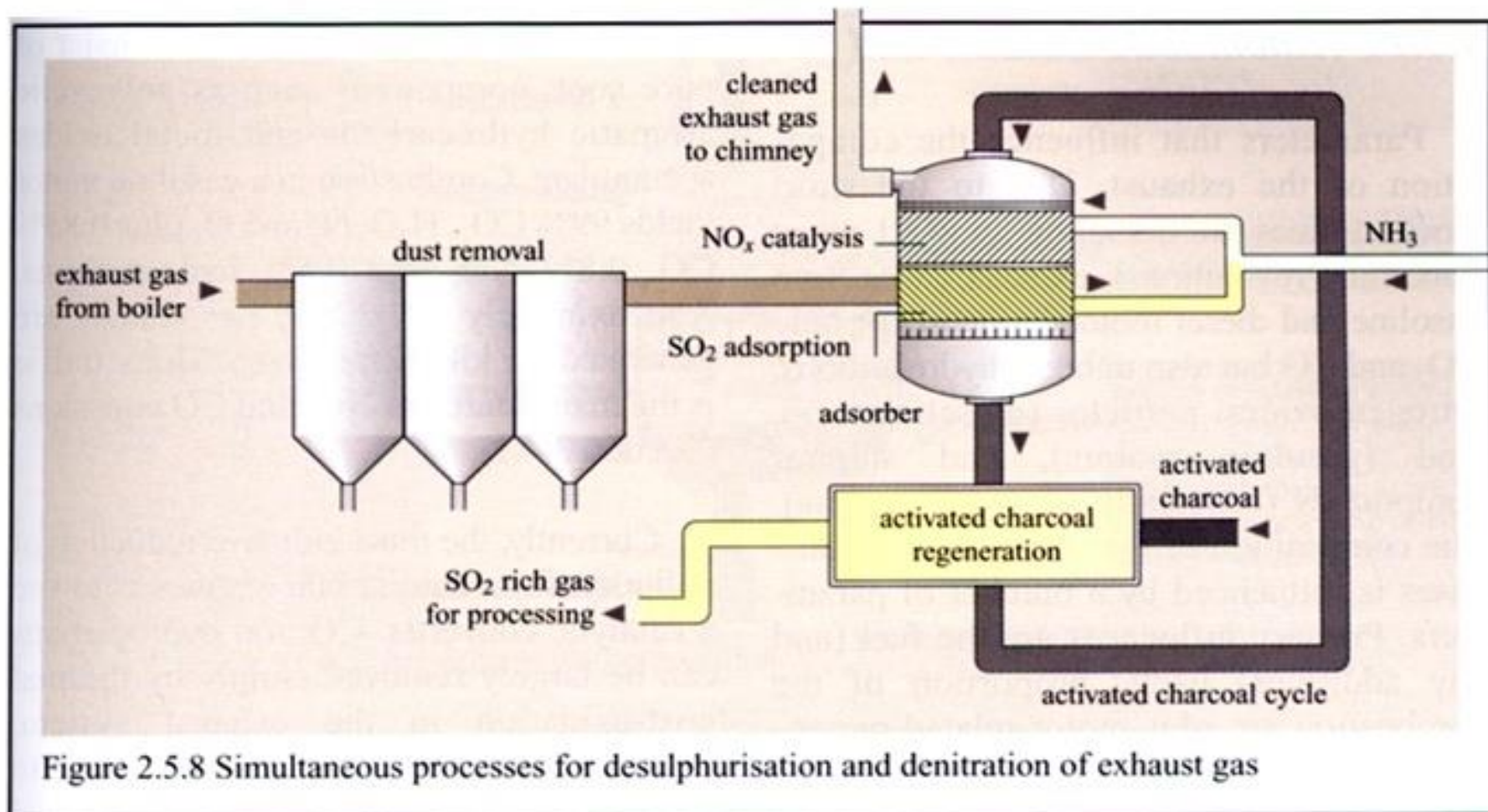
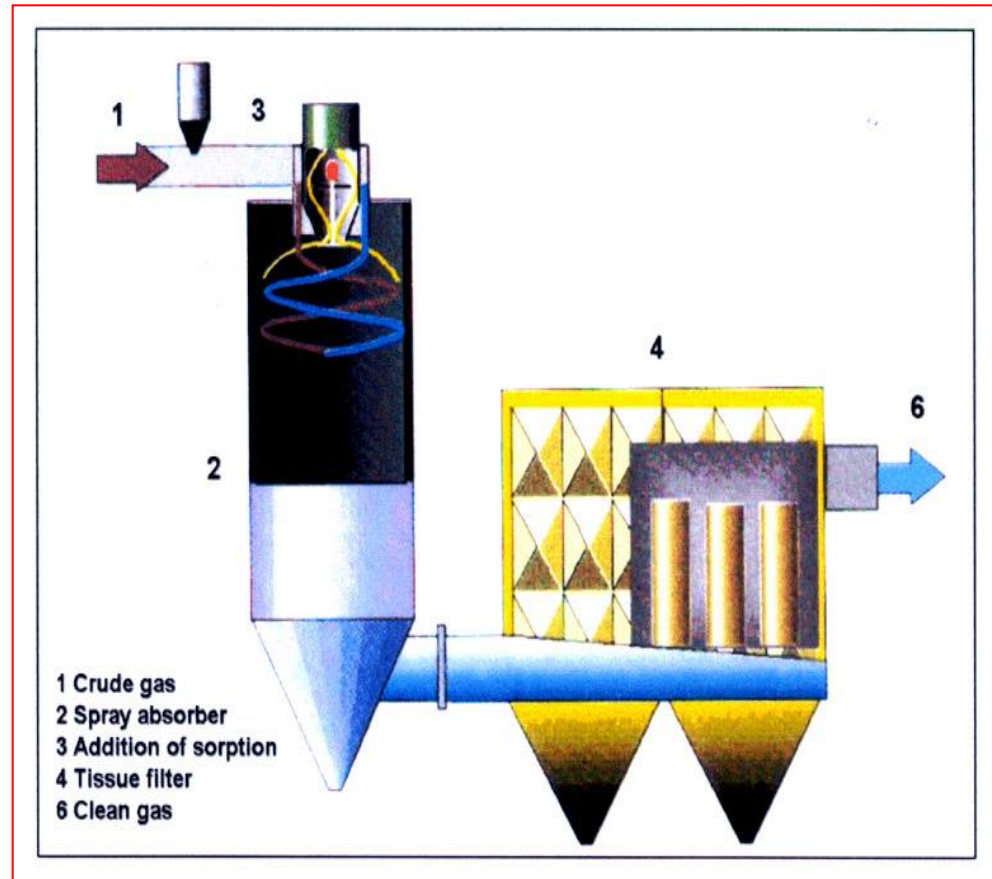


Figure 2.5.8 Simultaneous processes for desulphurisation and denitration of exhaust gas

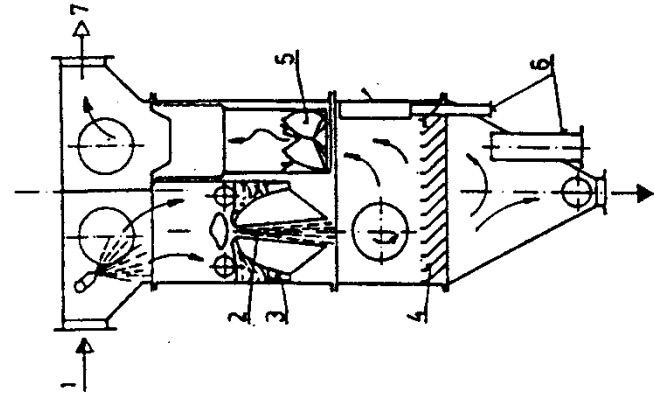
# Spray dry slurry

- ↪ Semi-wet scrubbing with injection of atomized hydrated lime slurry
- ↪ Removal of acid gases, dust and prevention of de-novo synthesis of dioxins and furans by rapid quenching
- ↪ No waste water

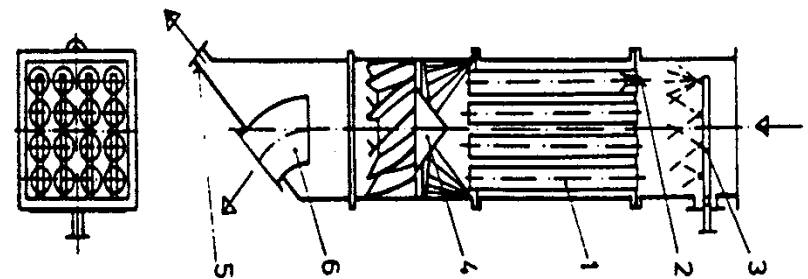


# Wet scrubbers

- ↪ Acid gas and dust removal
- ↪ Rapid quenching
- ↪ Two stage (water + lime)
- ↪ Catalytic oxidation in packed tower scrubbers (polypropylene embedded with carbon)
- ↪ Fine dust absorbers for specific dioxin separation

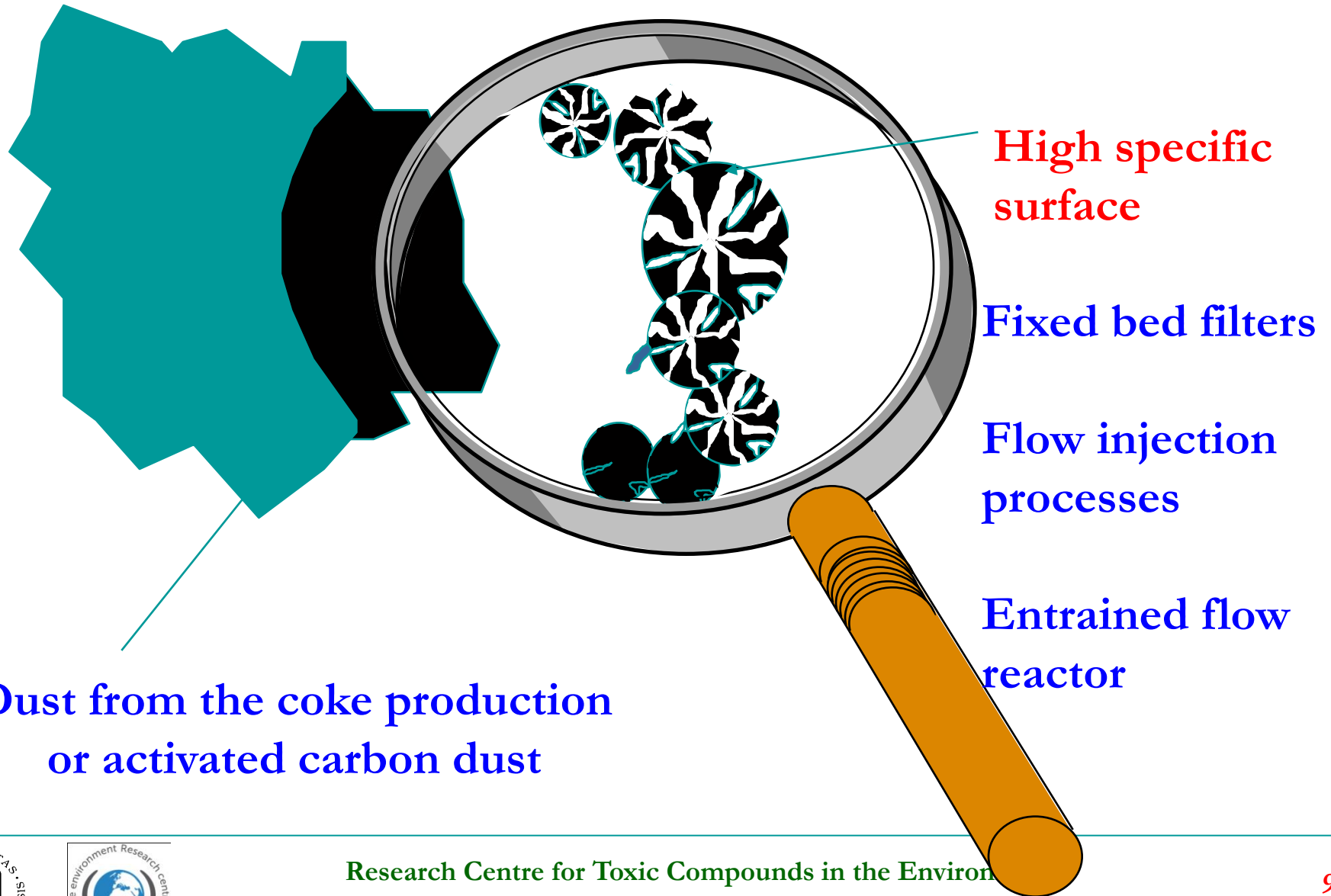


Obr. 52. Odlučovač s Venturiho trubicí obdélníkového průřezu



Obr. 51. Moký vířňkový odlučovač

# Sorption processes



Dust from the coke production  
or activated carbon dust

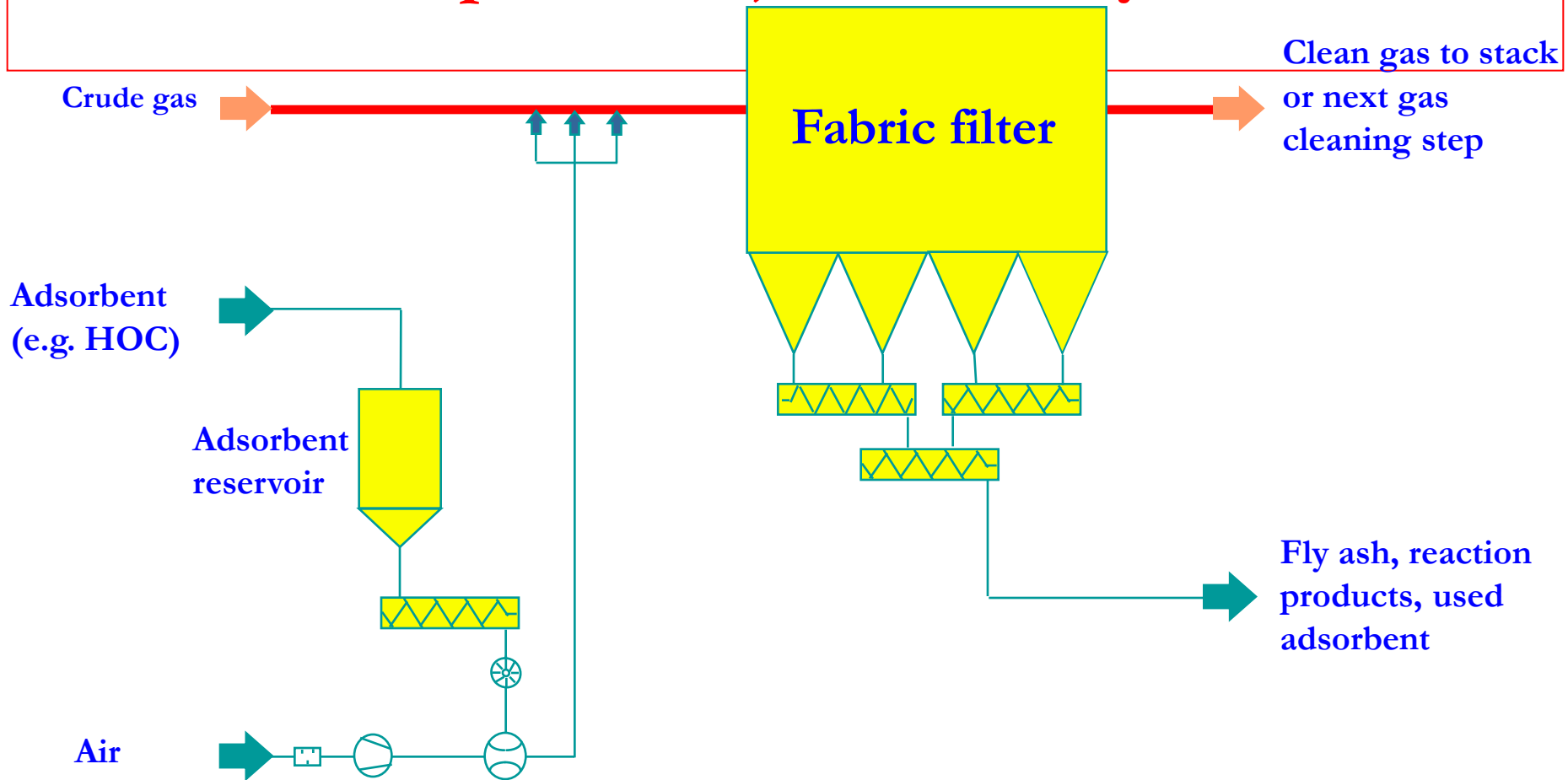
High specific  
surface

Fixed bed filters

Flow injection  
processes

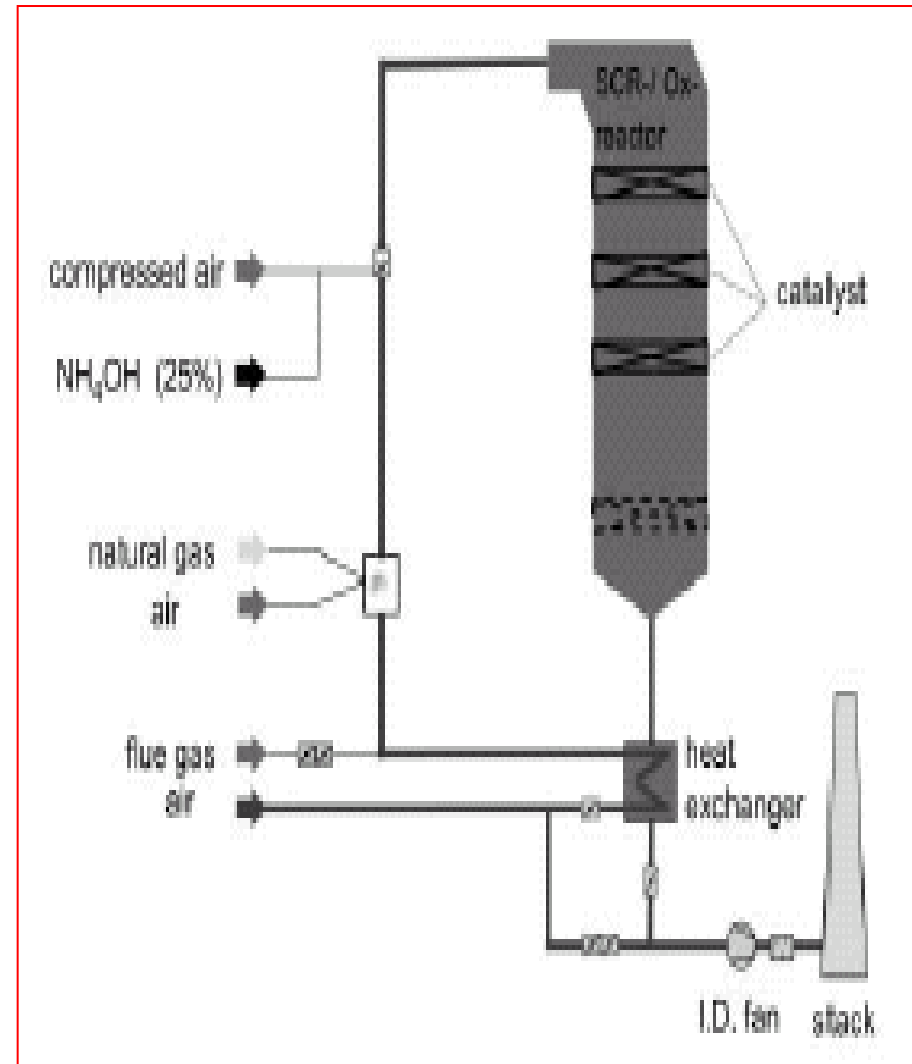
Entrained flow  
reactor

# POPs adsorption – injection of dry adsorbent



# Catalytic oxidation

- ↪ Pre-cleaned gas
- ↪ May be combined with DeNox
- ↪ Catalytic bag filters
- ↪ Easy operation and no residues



# Flue gas residue treatment

↪ Recycling

↪ Disposal to landfill

- ❖ Direct land filling
- ❖ Solidification (cement stabilization)
- ❖ Vitrification, melting and sintering
- ❖ Extraction and separation
- ❖ Chemical stabilization

↪ Incorporation into road making materials

↪ Valorization in salt or coal mines

# BAT - Residue Management Techniques

- ↪ Unlike bottom ash, APCD residuals including fly ash and scrubber sludges may contain relatively high concentrations of heavy metals, organic pollutants (including PCDDs/Fs), chlorides and sulfides.
- ↪ Mixing fly ash and FGT residues with bottom ash should be avoided since this will limit the subsequent use and disposal options for the bottom ash.



# BAT - Residue Management Techniques

↪ Treatment techniques for these residues include:

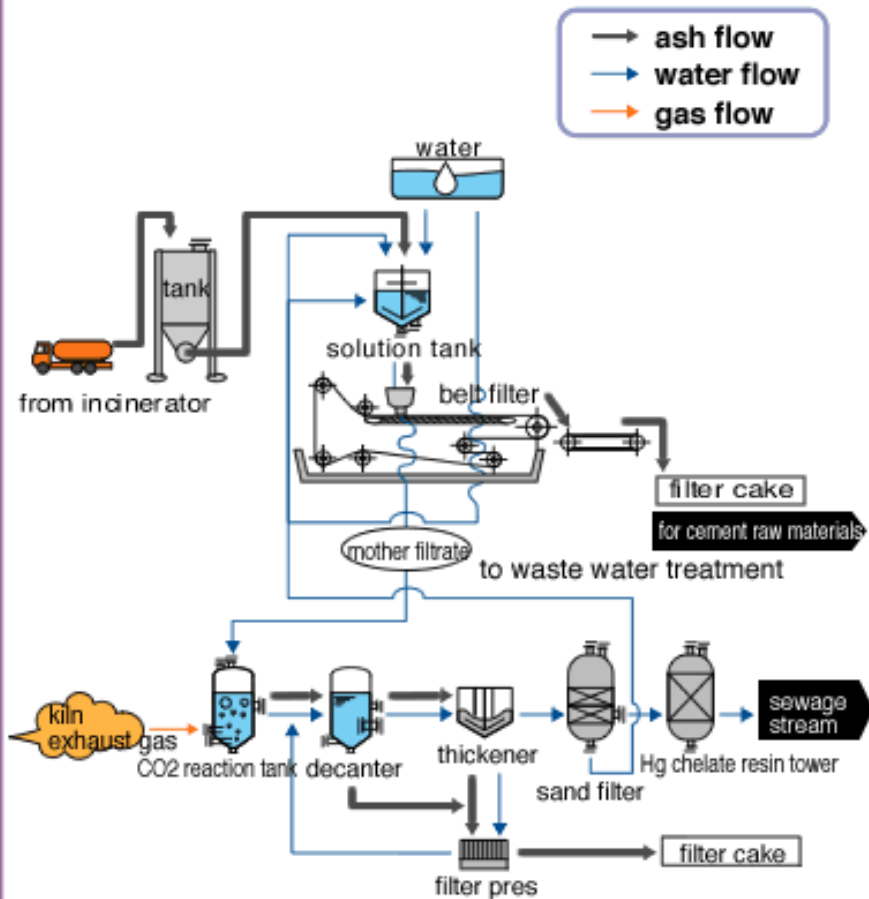
- ❖ **Cement solidification.** Residues are mixed with mineral and hydraulic binders and additives to reduce leaching potential. Product is landfilled.
- ❖ **Vitrification.** Residues are heated in electrical melting or blast furnaces to immobilize pollutants of concern. Organics, including PCDD/F are typically destroyed in the process.
- ❖ **Catalytic treatment** of fabric filter dusts under conditions of low temperatures and lack of oxygen;
- ❖ **The application of plasma** or similar high temperature technologies

# BAT - Residue Management Techniques

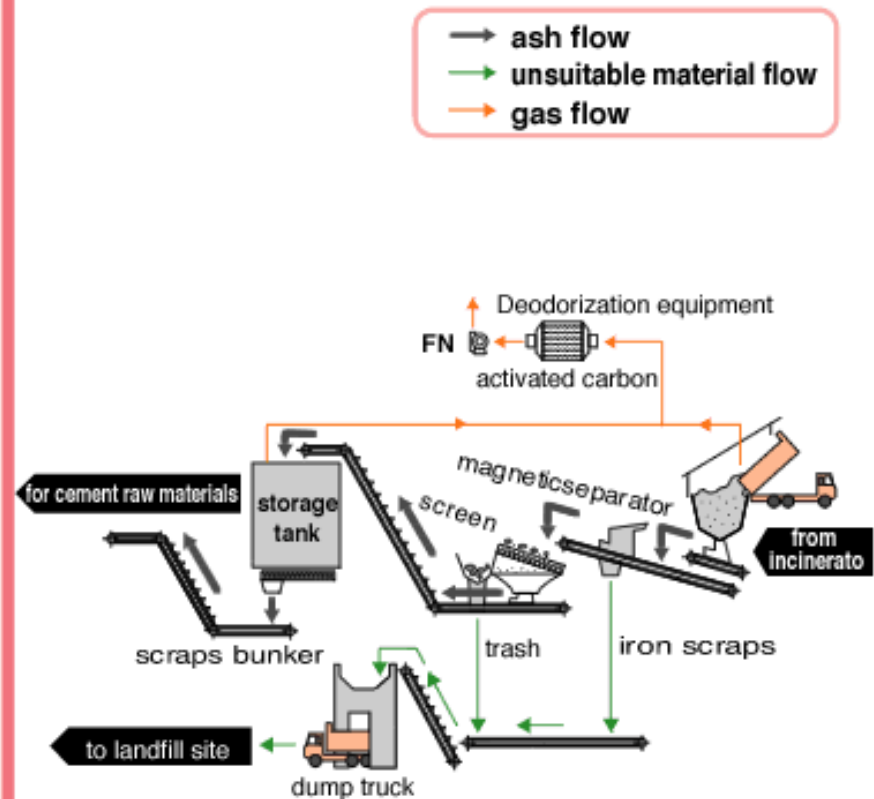
- ↪ **Fly ash and scrubber sludges** are normally disposed of in landfills set aside for this purpose. Some countries include ash content limits for PCDD/F in their incinerator standards. If the content exceeds the limit, the ash must be re-incinerated.

# Residue treatment

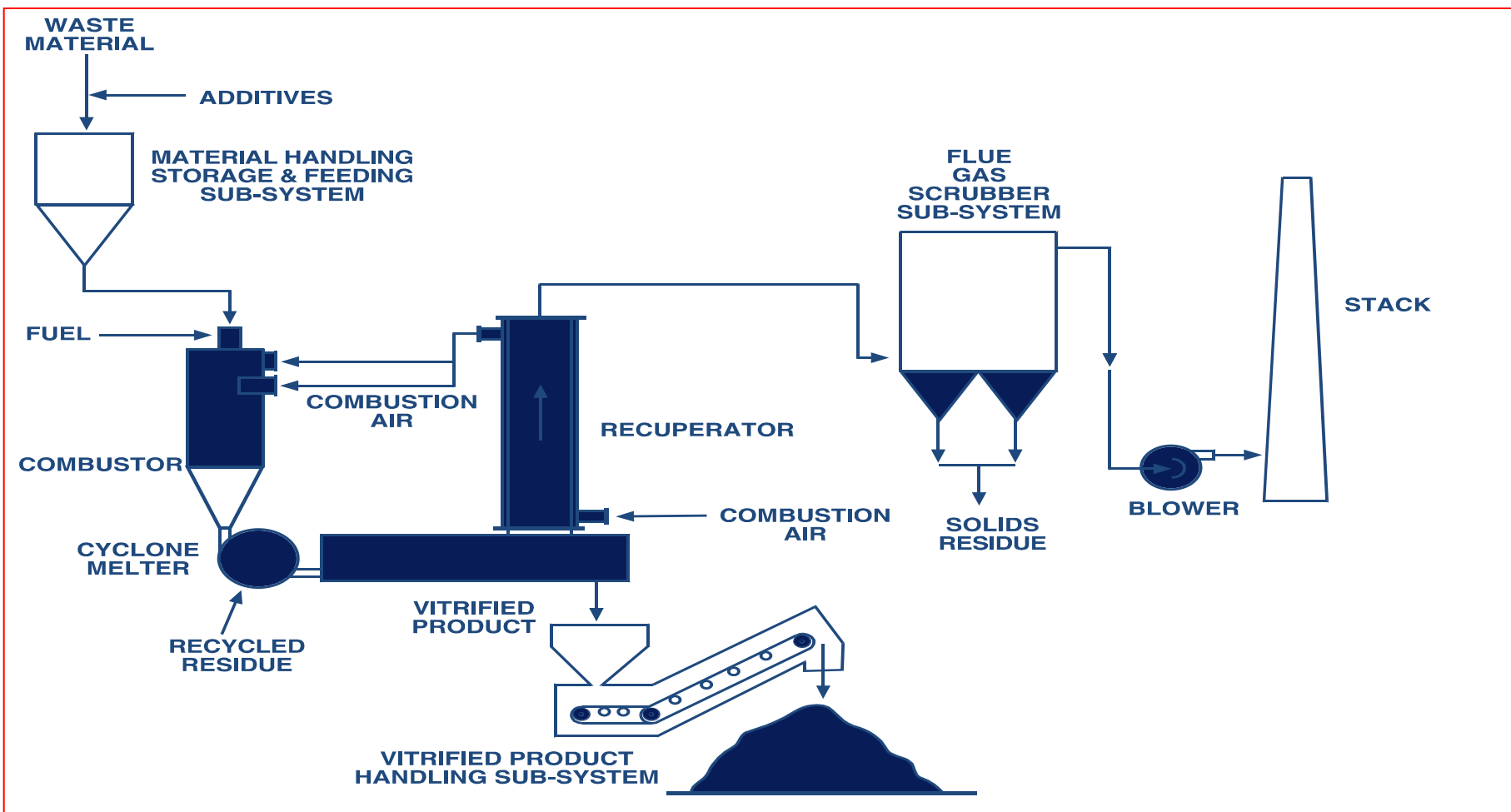
## Fly Ash Washing Process



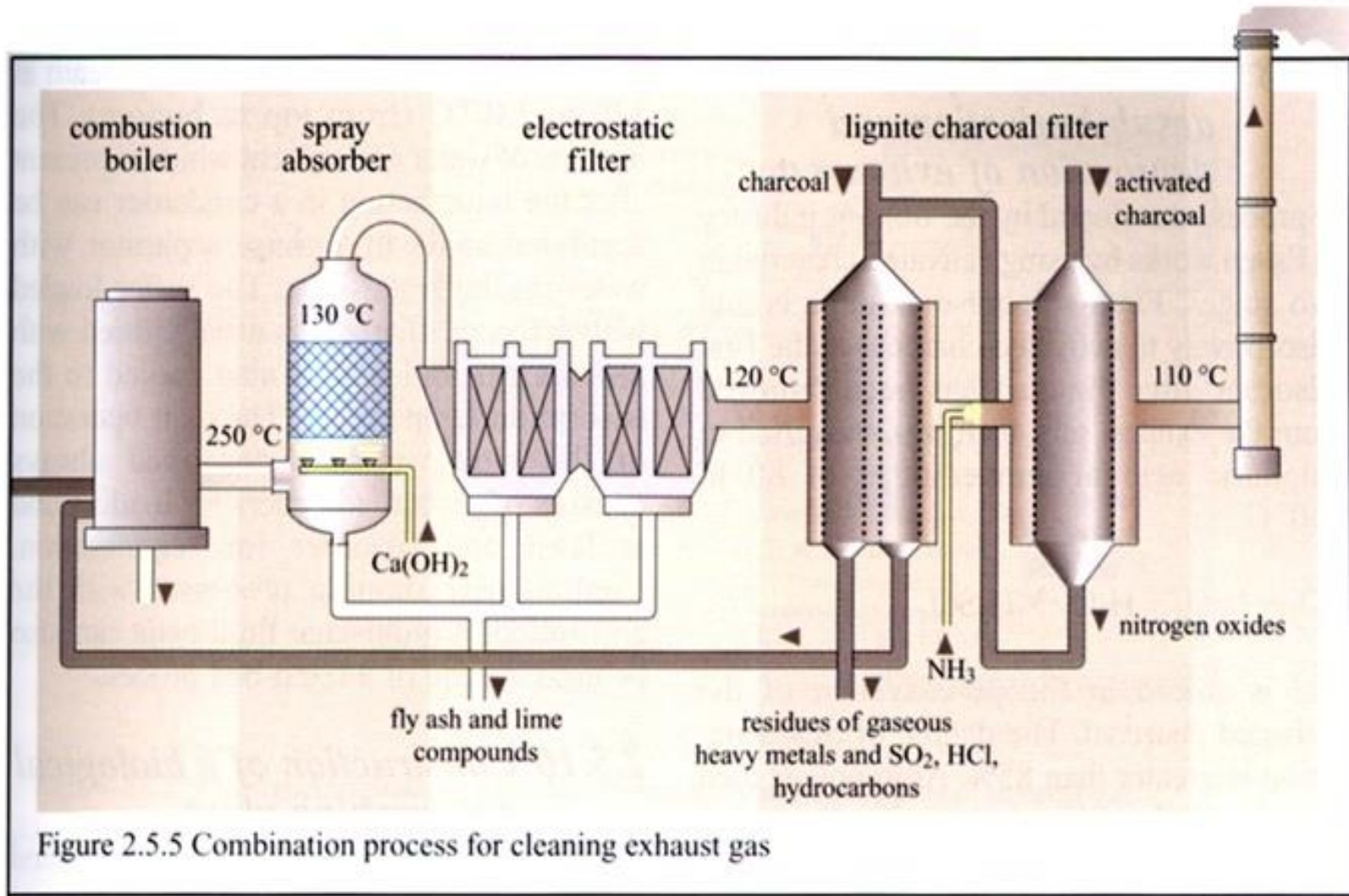
## Bottom Ash Pretreatment Process



# Flue gas residue treatment



# Combination flue gas treatment



# Medical waste incineration

Infectious/biological health care waste, sharps and body parts

- ↪ **Alternatives:** sterilization (autoclaving - steam), microwave, alkaline hydrolysis; waste minimization by segregating the hazardous waste from the municipal-like w. (75-90%)
- ↪ **Purpose** of waste incineration: destruction of organic matter, disinfection and volume reduction
- ↪ **BAT/BEP/BACT:** prevent or minimize POPs releases, proper waste handling, ensure good combustion, avoid formation conditions, capturing POPs that are formed and handling residues appropriately
- ↪ **Achievable performance levels:** below-0,1 ng TEQ.Nm<sup>-3</sup>

# Medical waste management

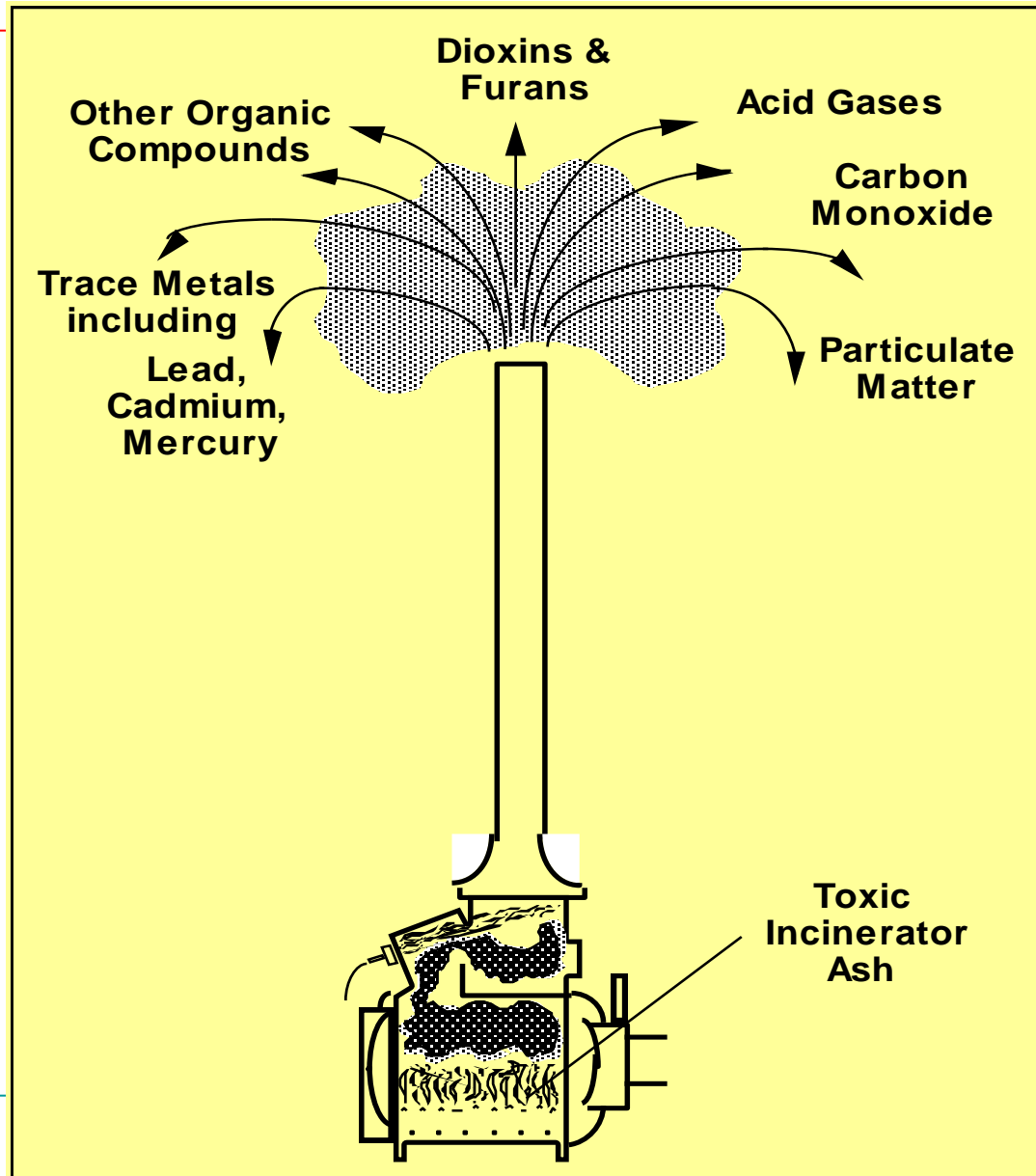
- ↪ **Segregation** (must take place at source to avoid secondary sorting)
- ↪ **Waste minimization** (replace disposable materials with reusables where feasible - Basel Convention Secretariat 2002, WHO 2000)
- ↪ **Training of personnel** (management from generation to disposal; responsibilities)
- ↪ **Collection at the site of waste generation** (proper containers/bins, packaging, labeling, sterilizing in bags)
- ↪ **Transport to the intermediate storage area** (proper storing conditions, protective cloths, clear routes, avoid package damage)

# BAT for thermal treatment

- ↪ **Pyrolysis + afterburner + APC**
- ↪ **Rotary kiln + afterburner + APC**
- ↪ **Adapted grate incinerator + APC**
- ↪ **Fluidized bed incinerator + APC**
- ↪ **Modular system (two chambers: starved/excess O<sub>2</sub> conditions +APC)**
- ↪ **APC:**
  - ❖ **Separation of dust and NV heavy metals (cyclones + filters)**
  - ❖ **Removal of HCl, HF, SO<sub>2</sub> and mercury (dry/wet adsorption, wet scrubbing)**
  - ❖ **Removal of NO<sub>x</sub> (primary measures, SCR, SNCR)**
  - ❖ **Reduction of organic emissions (primary measures, filtering, activated coke, catalytic oxidation)**
- ↪ **Waste: fly ash, slag, waste water treatment filter cake, gypsum, loaded activated carbon**

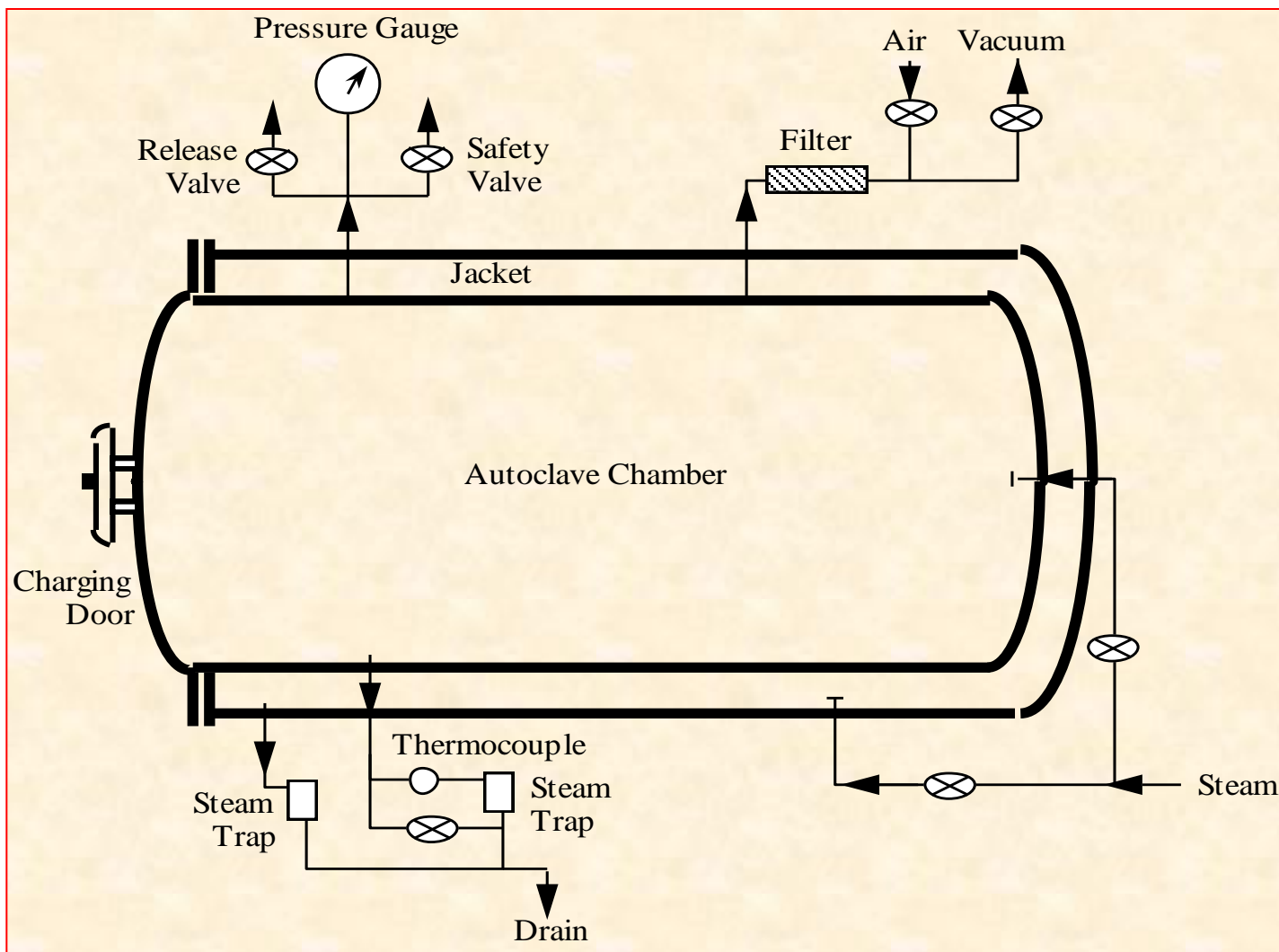


# Potential releases



<http://recetox.muni.cz>

# Autoclave

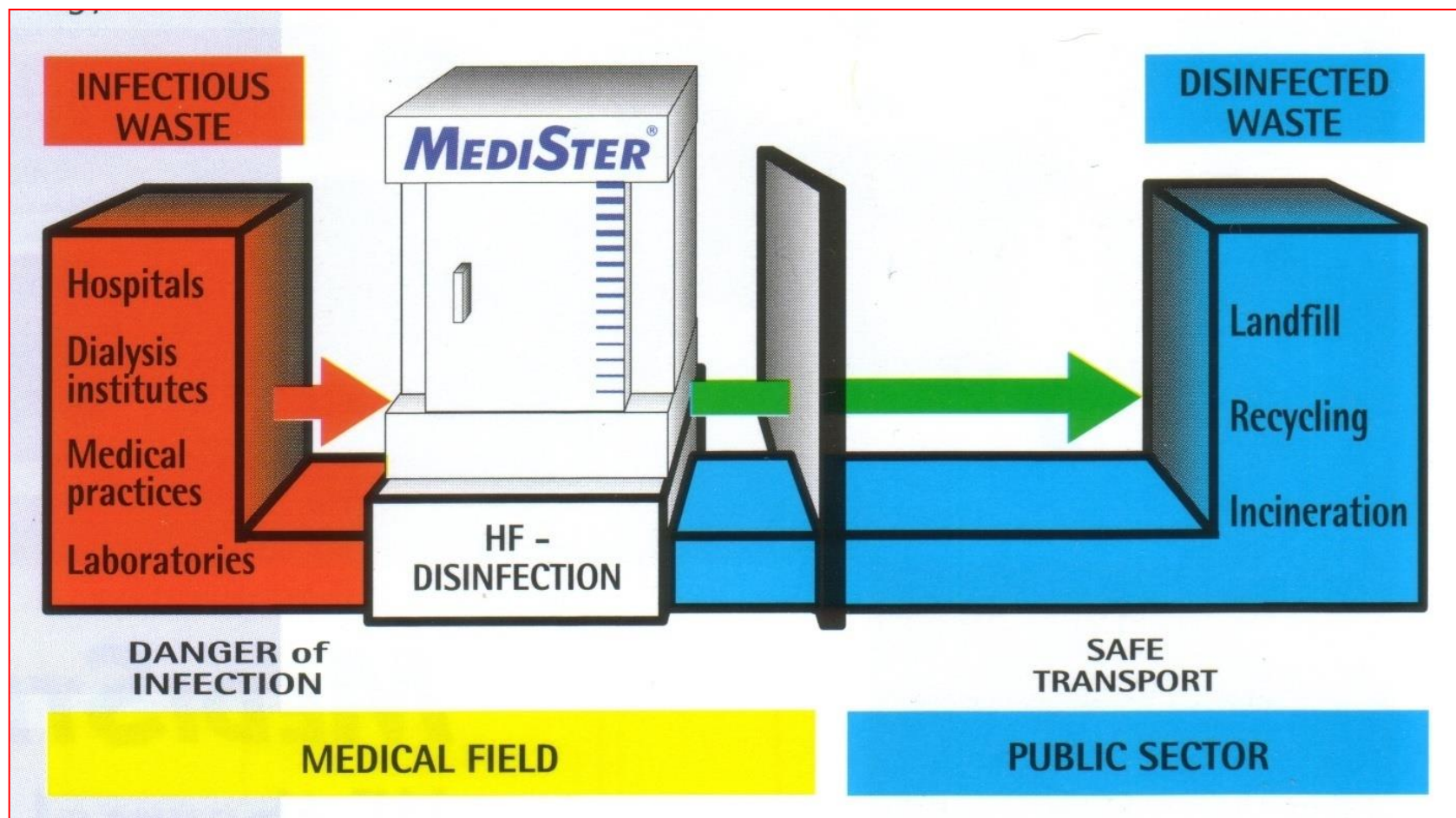


# Advanced autoclave



135 -140 °C  
270 - 300 kPa  
20 minutes

# Microwave disinfection

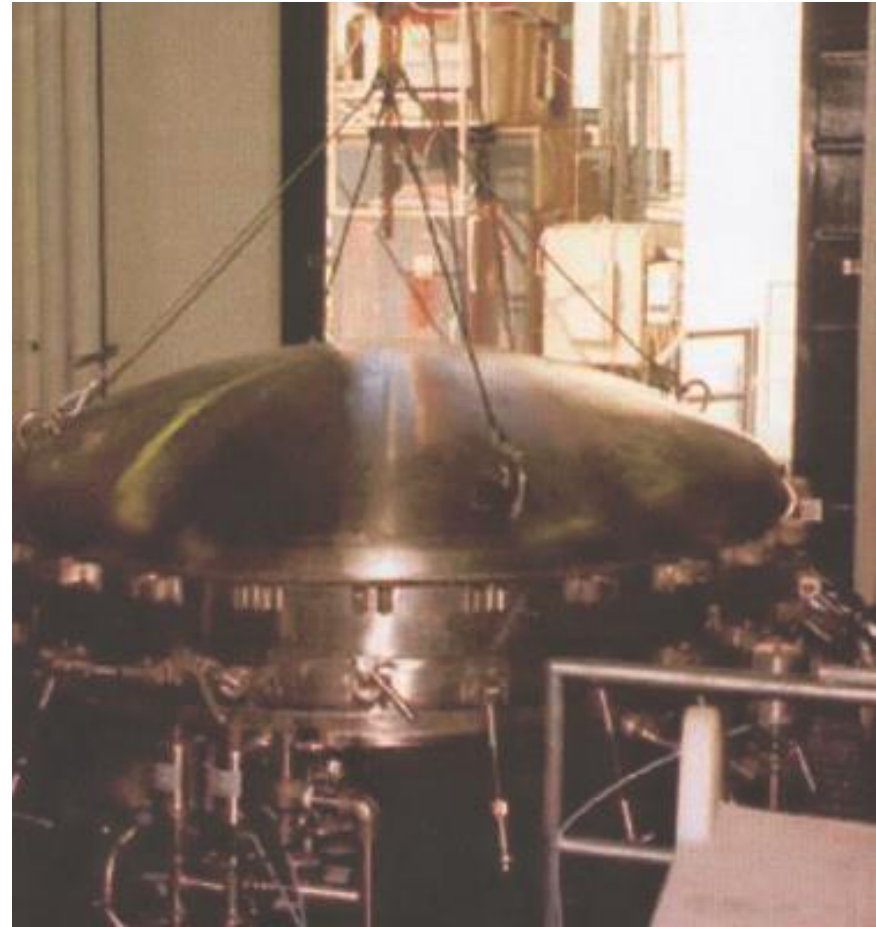


Source: Meteka, Austria

# Incineration vs. autoclaving (20 - 45 Kg/h)

Component price	Incineration	Autoclave
Basic equipment	150 000	70 000
Instalation	22 500	6 500
Measures to meet the US EPA limits	194 500	0
Electric steam generator	0	16 000
Monitoring and testing	16 600	2 400
<b>TOTAL</b>	<b>\$ 383 600</b>	<b>\$ 93 100</b>

# Alkaline hydrolysis



Source: Waste Reduction by Waste Reduction, Inc. (WR2), Indianapolis, Indiana

# Cement Kilns

- ↪ Another technology which is similar to incineration is represented by **cement kilns** used quite widely to destroy mainly **liquid PCB-containing wastes**.
- ↪ **The PCB-containing liquids are introduced with the fuel in the cement kiln**, thereby allowing the conventional fuel to be partially replaced by the liquid waste. This latter has often quite a high calorific value, and thus may be welcomed by cement kiln operators as representing a cheaper source of energy for their process.

# Cement Kilns

- ↪ The operating conditions of cement kilns burning chlorinated wastes are typically subject to very close control by the appropriate authorities to ensure that levels of dioxin and furan which might be present in the off-gases are kept within the regulatory norms.
- ↪ The ability of these kilns to accept PCBs or any other chlorinated mixture is dependent to a considerable extent on the level of chlorine in the material, as more highly chlorinated materials present increasingly difficult complications.



# Cement kilns firing hazardous wastes

- ↪ **Purpose:** clinker production. Firing waste aims at energy recovery and substitution of fossil fuels along with HW disposal
- ↪ **Secondary fuel:** tires, waste oils, sewage sludge, rubber, waste wood, plastics, paper waste, paper sludge, animal meal, spent solvents
- ↪ **BAT:** Primary measures in a cement kiln are sufficient for destruction of chlorinated HW
- ↪ **BEP/BECT:** Prevention of de-novo synthesis in the off-gases; temperatures below 250°C at ESP inlet
- ↪ **Performance:** PCDDs/Fs concentration < 0,1 ng TEQ.Nm<sup>-3</sup> destruction/removal efficiency for PCBs is 99,995% and better (in USA destruction/removal efficiency of 99,9999% is required)

# Cement kiln co-processing ensures

## Sufficient:

- ↻ temperature
- ↻ oxygen
- ↻ residence time
- ↻ mixing conditions
- ↻ alkaline environment

# Hazardous waste incineration

	Requirements		Performance	
	EU	USA	Dedicated incinerators	Cement kiln
Temperature	850 -1100 °C	850 – 1600 °C	900 –1200 °C	1450 – 2000 °C
Residence time	≥ 2 seconds	≥ 2 seconds	0,3 – 4 seconds	4-8 seconds
Oxygen availability	3 – 6 %	2 – 3%	> 4 %	> 4%
Turbulence/mixing	Yes	Yes	Yes	Yes
Thermal stability	Auxiliary burners	Auxiliary burners	Auxiliary burners	Thermal buffer
Exit gas cleaning	ELVs	ELVs & DRE	Advanced	EP/bag etc & lime scrubbing

# Proposed requirements for sound disposal of POPs

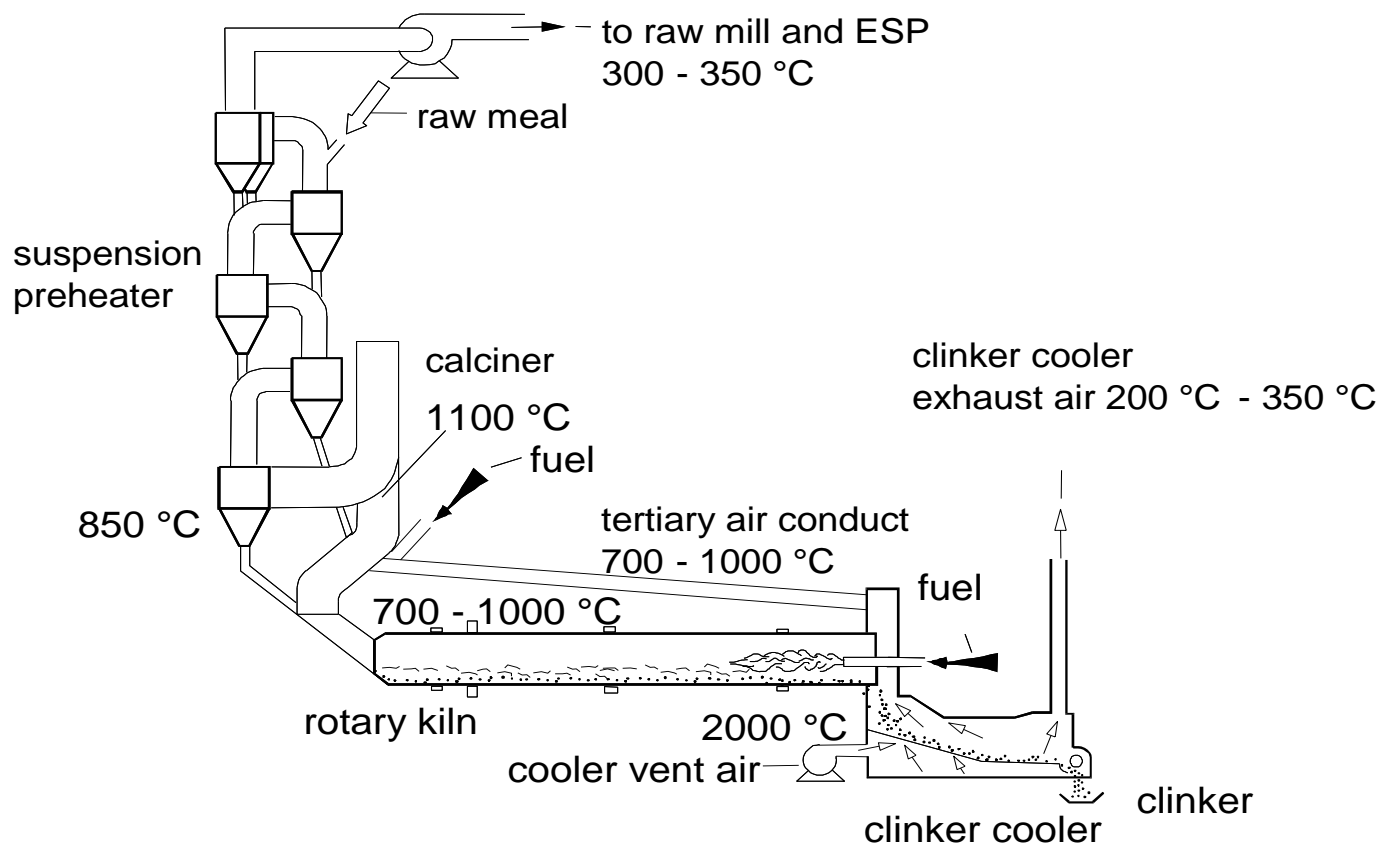
The following disposal operations, as provided for in Annex IVA and IVB of the Basel Convention, should be permitted for the purpose of destruction and irreversible transformation of the POP content in wastes when applied in such a way as to ensure that the remaining wastes and releases do not exhibit the characteristics of POPs (many are still pilot demonstration)

Technique	DE/DRE (%)	Cost
Alkali reduction	No	
Base catalyzed decomposition	99.99-99.9999	↑
Cement kiln co-processing	99.99-99.9999	←
Gas phase chemical reduction	99.99-99.9999	↑
Hazardous waste incineration	99.99-99.9999	↑
Mediated electro chemical oxidation	99.995	
Silver oxidation	No	
Plasma arcs	99.99-99.9999	↑
Super critical water oxidation	No	

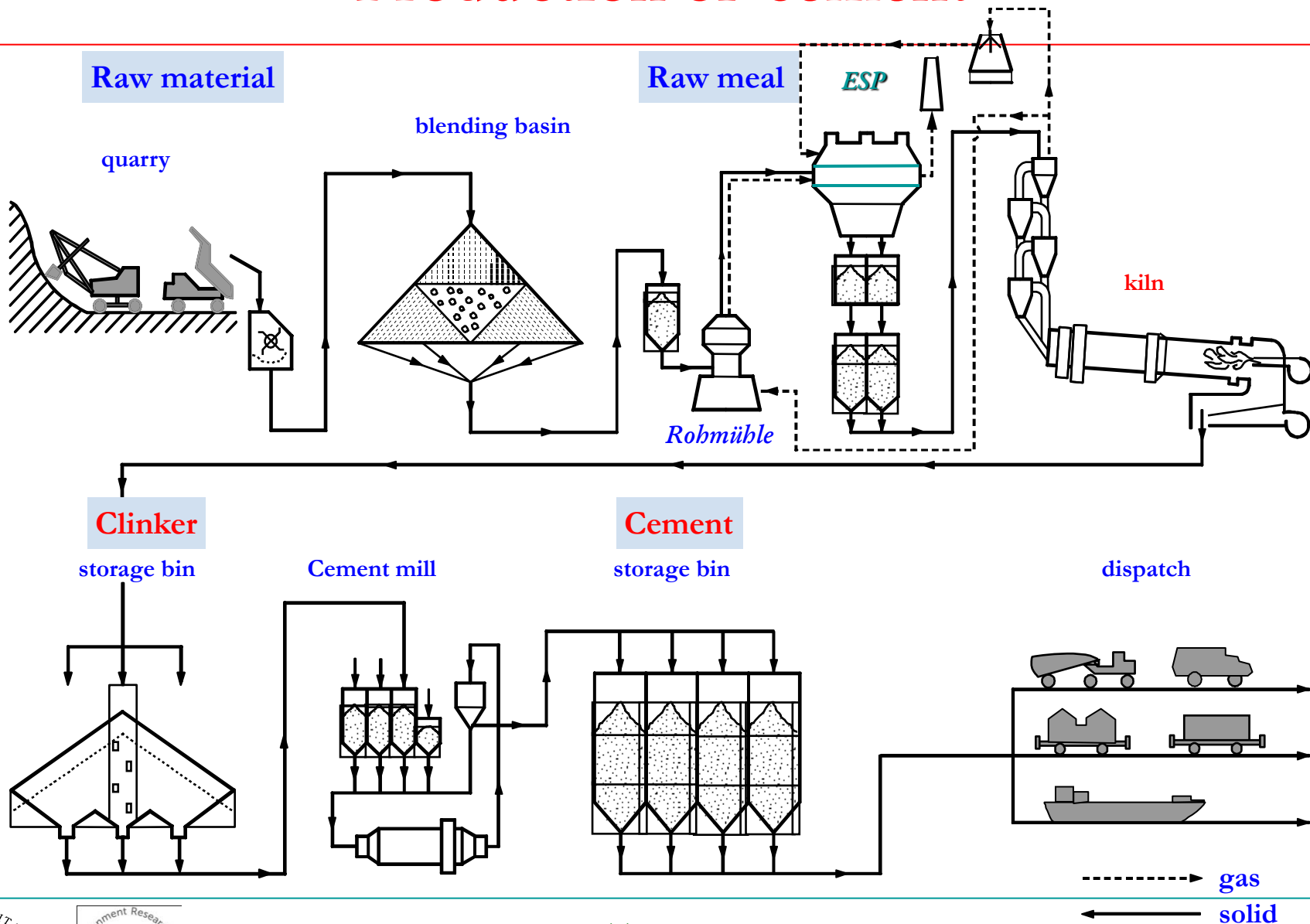
**Are cement kilns able to destroy POP's in an irreversible manner and comply with the requirements of the Stockholm Convention?**



# Temperature conditions in a cement kiln



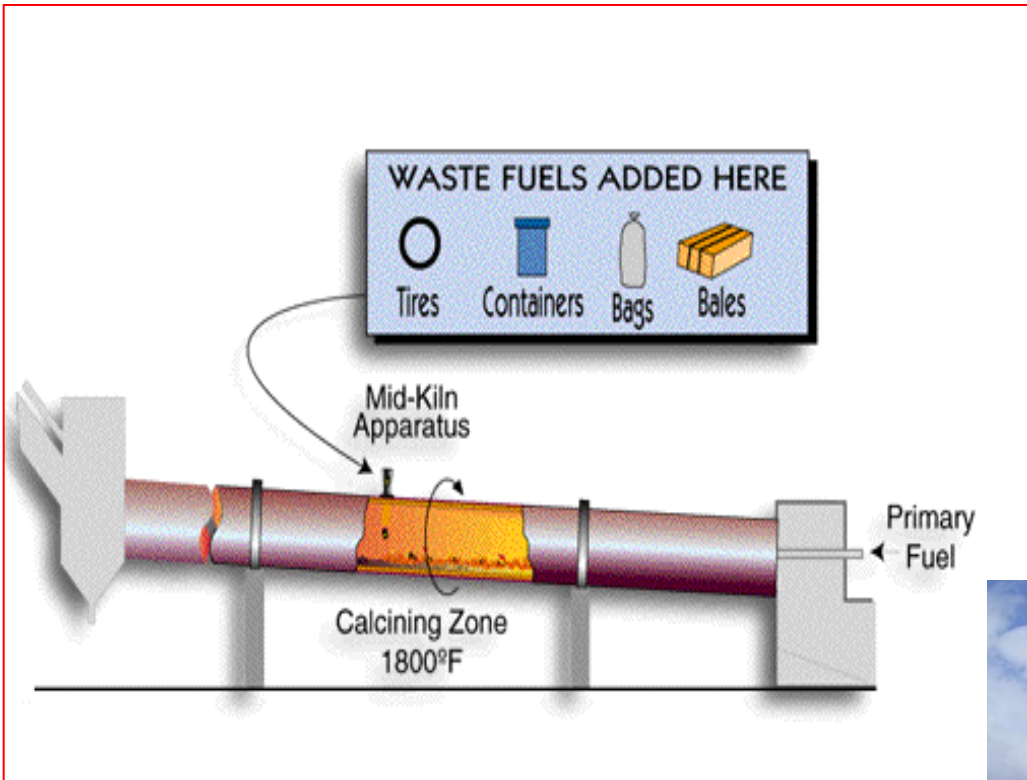
# Production of cement



Research Centre for Toxic Compounds in the Environment

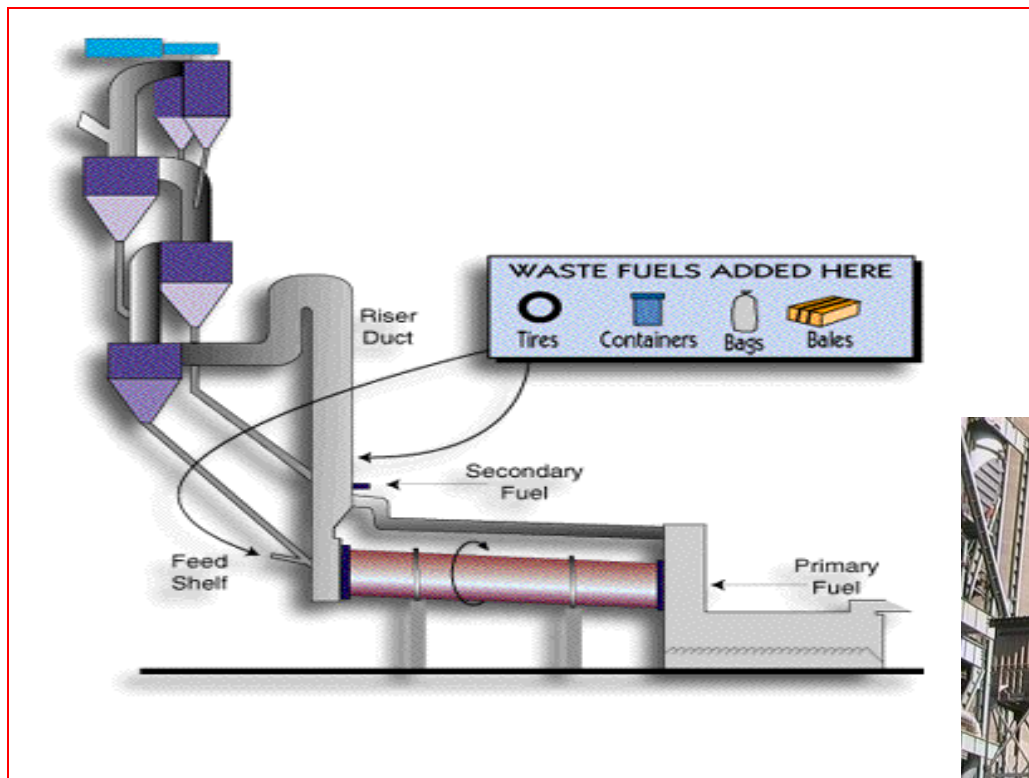
<http://recetox.muni.cz>

# Long wet kiln

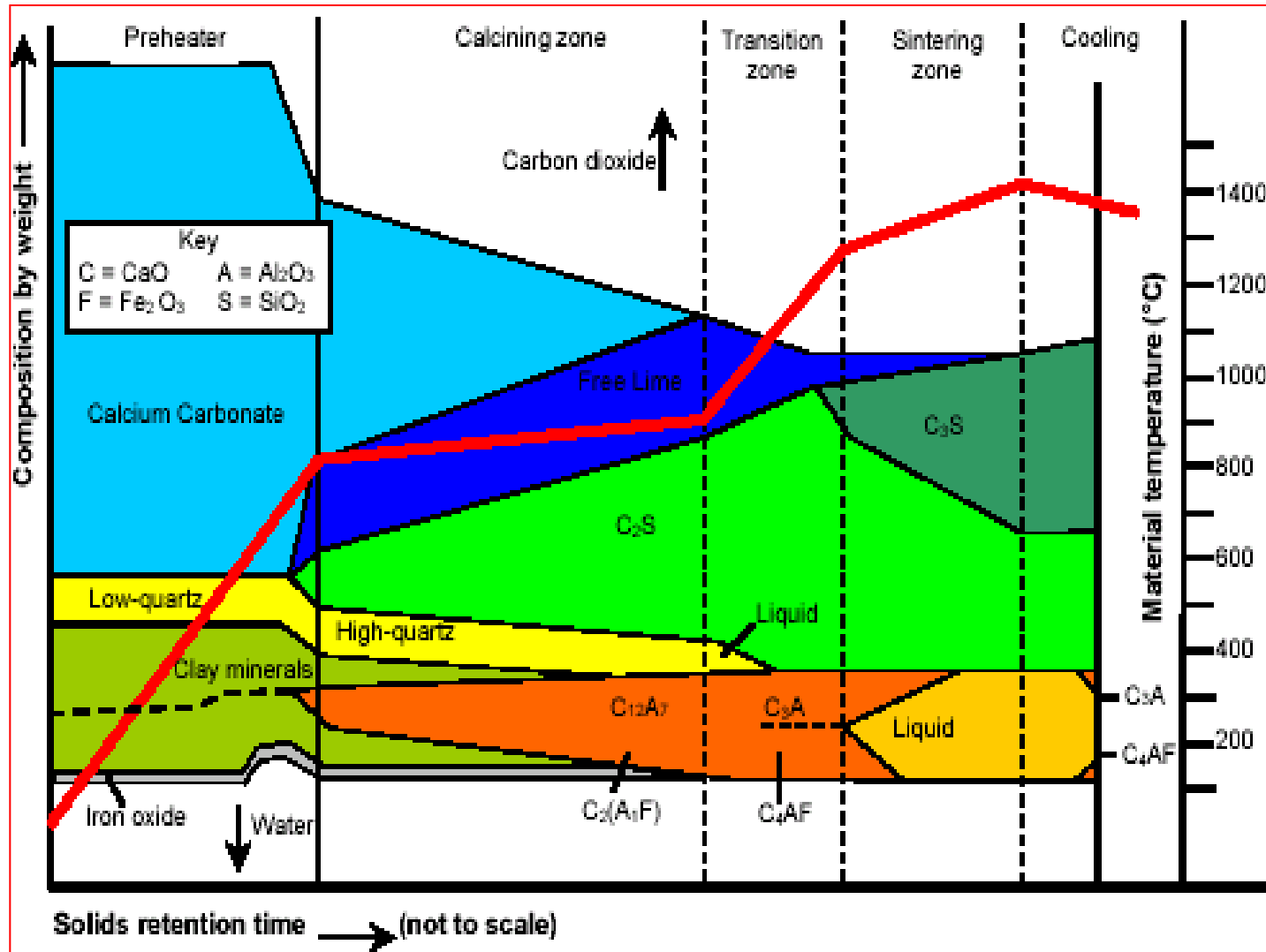




# Dry preheater & precalciner kiln



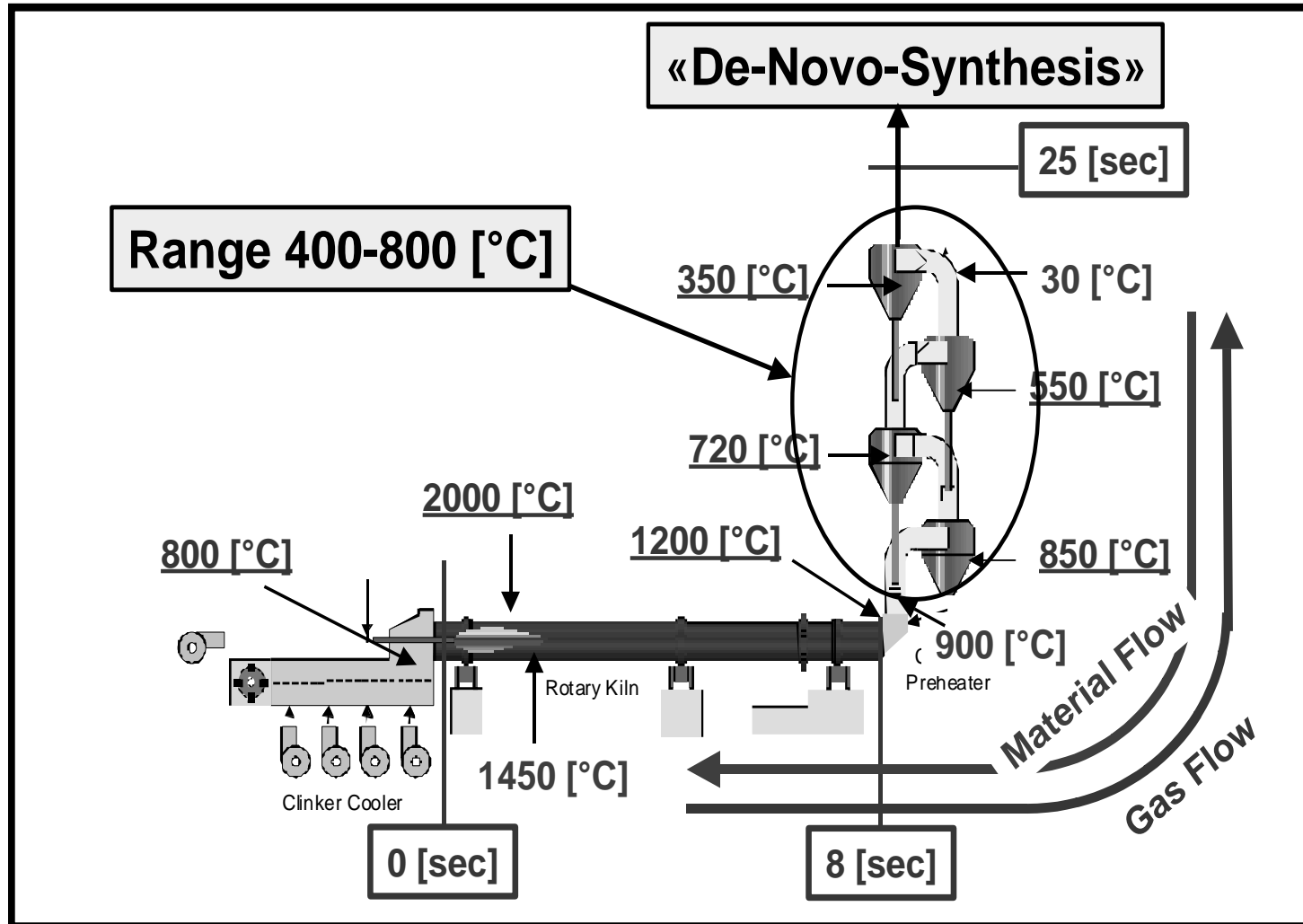
# Processes in cement kiln



# Main burner



# Temperatures and retention time in a preheater cement kiln



# Cement industry



World Business Council for  
Sustainable Development  
Cement Sustainability Initiative

**One of the main routes towards sustainability in the cement industry is to reduce the use of virgin raw materials and non-renewable fossil fuel and replace with alternative fuels and raw materials.**

# Co-processing of wastes in cement kiln



Toxi  
p://

# Co-processing of hazardous wastes in cement kiln

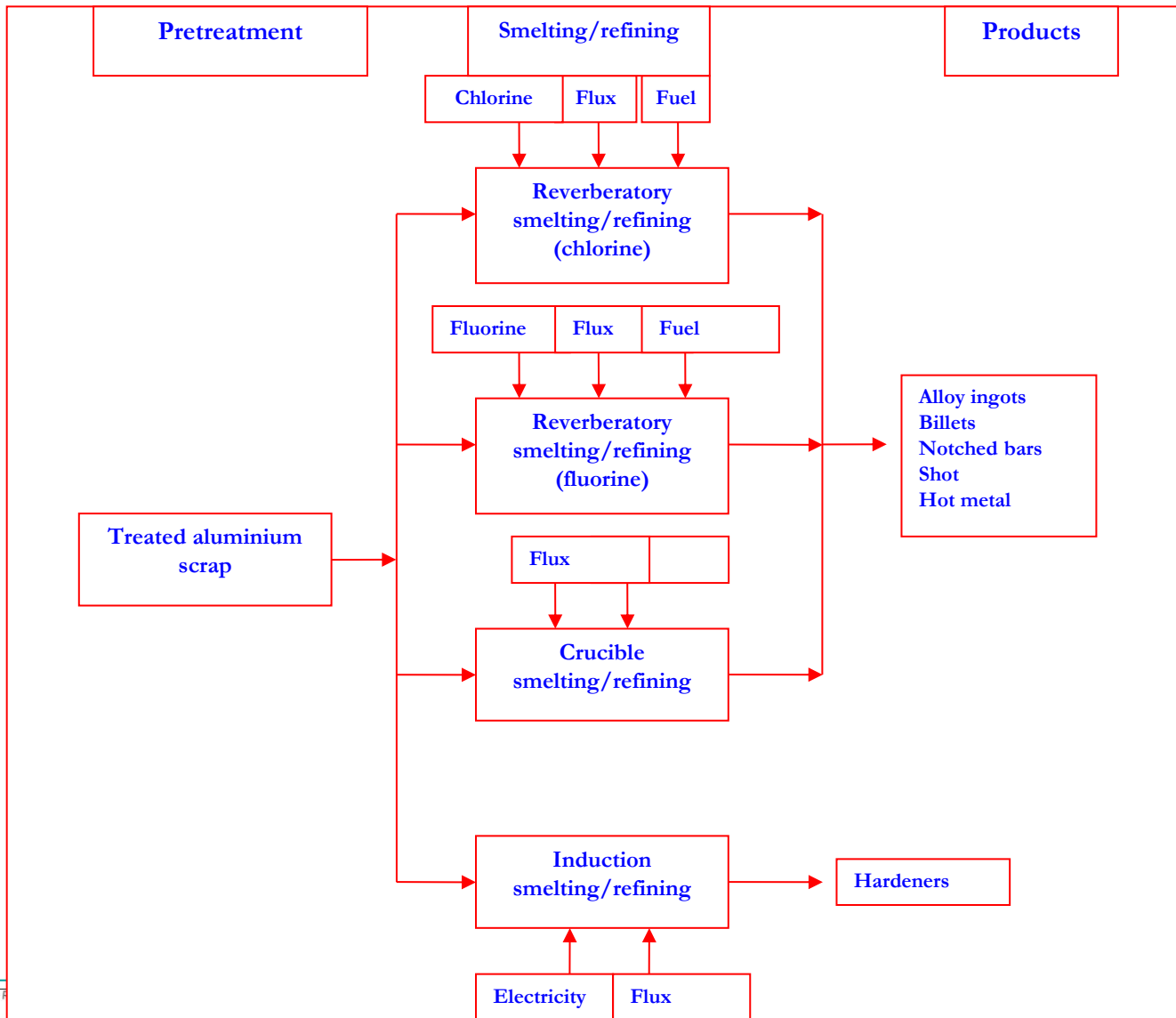
- ↪ ...is accepted to be a suitable treatment option in current European, US and others regulation (needs to comply with ELV's and DRE requirements).
- ↪ More than 10 million tons of Hazardous Wastes is co-processed in cement kilns world wide annually.

# Secondary aluminum production

- ↪ **Purpose:** production of aluminum from used products to recover metals by pretreatment, smelting and refining
- ↪ **BAT / BEP / BECT:** Pre-sorting and treatment of scrap, high temperature advanced furnaces (above 850°C), oil-chlorine-free feeds, closed/sealed systems, afterburners with rapid quench, activated carbon adsorption and fabric filters, prevention of de-novo synthesis in the off-gases; temperatures below 250°C at filter inlet
- ↪ **Performance:** dioxin/furan concentration < 0.1 ng TEQ.Nm<sup>-3</sup>



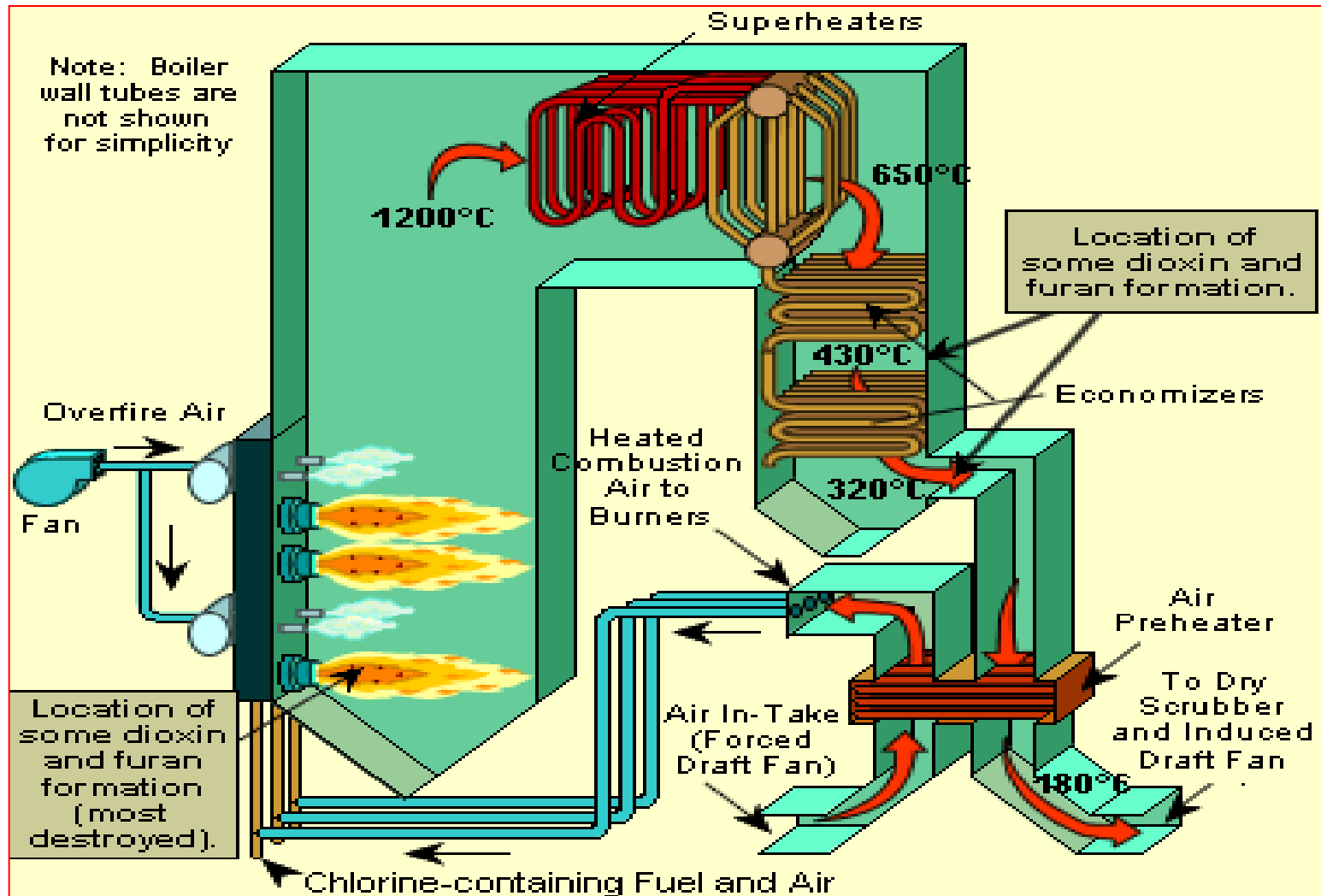
# Secondary aluminum production



# Fossil fuel fired utility and industrial boilers

- ↪ **Purpose:** Burn fuel to heat water or to produce steam for use in electricity generation or in industrial processes
- ↪ **BAT / BEP / BECT:** Maintenance of efficient combustion conditions, measures to avoid contamination of fuels with PCBs, HCB or chlorine as well as dioxin formation catalysts, use appropriate gas cleaning methods, prevention of de-novo synthesis in the off-gases; temperatures below 250 °C at filter inlet , strategies for disposal, storage or use of collected ash
- ↪ **Performance:** dioxin/furan concentration significantly lower than 0.1 ng TEQ.Nm<sup>-3</sup>

# Possible PCDD/PCDF formation



# Firing installations for wood and other biomass fuels

- ↪ **Purpose:** Energy conversion
- ↪ **BAT / BEP / BECT:** Fuel quality control, maintenance of efficient combustion conditions, measures to avoid contamination of fuels with PCB, HCB or chlorine as well as dioxin formation catalysts, use appropriate gas cleaning methods, prevention of de-novo synthesis in the off-gases; temperatures below 250 °C at filter inlet, strategies for disposal, storage or use of collected ash
- ↪ **Performance:** dioxin/furan concentration significantly lower than 0.1 ng TEQ.Nm<sup>-3</sup>

# Sound practices

## MODERN WASTE MANAGEMENT SYSTEMS

- ↻ Resource use reduction
- ↻ Reuse
- ↻ Recovery/recycling
- ↻ Composting
- ↻ Environmentally sound landfilling
- ↻ Incineration using BAT

# Barriers to use alternatives

- ↪ Lack of education
- ↪ Lack of government will to reduce dependence upon open burning to accomplish goals
- ↪ Open burning is an integral part of local agriculture
- ↪ Lack of alternative machinery or process or necessary infrastructure
- ↪ Cost of alternatives
- ↪ Economic instruments
- ↪ Demonstration projects

# Residential combustion sources

- ↪ **Purpose:** Small scale energy conversion for household heating and cooking
- ↪ **BAT / BEP:** High quality efficient combustion (combustion chamber temperature, turbulence of the burning gases, residence time, excess oxygen and fuel type); use of more efficient improved stoves (improving also indoor air quality); no use of household waste as fuel
- ↪ **Performance:**  $< 0.1 \text{ ng TEQ.Nm}^{-3}$

# Residential combustion

- ↪ **PCDD/PCDF formation:** wood < coke < coal < biomass << co-combustion of wastes
- ↪ **Incomplete combustion**
- ↪ **Central heating or individual stoves**
- ↪ **No possibility for emission control**
- ↪ **Developing countries:**
  - ❖ **Very simple stoves**
  - ❖ **No chimney/ventilation, resulting in indoor pollution**
  - ❖ **Significant health effects on women and children**
- ↪ **Global Partnership for Clean Indoor Air (2003)**  
<http://www.pciaonline.org/> and <http://www.rwedp.org/>



# BAT/BEP

## BAT:

- ↪ Good mixing of gas and air (high turbulence)
- ↪ Sufficient residence time in the hot zone
- ↪ Minimal disturbance of the glow bed and homogenous distribution of the primary air
- ↪ Minimal residence time in the temperature range between 180 – 500 °C and minimal dust deposition ability
- ↪ Stack kept clean and free of soot by ensuring complete combustion and regular cleaning

# BAT/BEP

Great attention should be paid to regular maintenance of the appliances in order to prevent/discover and repair potential problems, such as:

- ↪ Cracked heat exchanger
- ↪ Not enough air to burn fuel properly
- ↪ Defective/blocked flue
- ↪ Maladjusted burner
- ↪ Defective grate
- ↪ Green or treated wood
- ↪ Inappropriate fuel (other than required by the constructor; residential waste)

# BAT/BEP

- ↪ **Ventilation to reduce indoor pollution and ensure proper combustion**
- ↪ Hood fan over the stove
- ↪ Ensure sufficient air flow into the house
- ↪ The vent is connected and unblocked without cracks or holes
- ↪ Ad more air (opening the stoker door)
- ↪ Smoke and soot indoors are signs of that the stove is releasing pollutants into the indoor air
- ↪ **Inspection and maintenance at regular intervals**

# BAT/BEP

## Correct use of appliances and fuel

- ↪ Understand and follow the operating instructions and to use the recommended kind of fuel
- ↪ Burn hardwood rather than softwood (hotter/les creosote)
- ↪ Avoid green wood and wet wood
- ↪ Never burn any kind of waste, treated wood

## Education awareness and training programmes

- ↪ Programmes for sellers and buyers of the stoves
- ↪ Proper information on potential hazards to human health
- ↪ Education and awareness on the appropriate use of fuels and general BEP issues

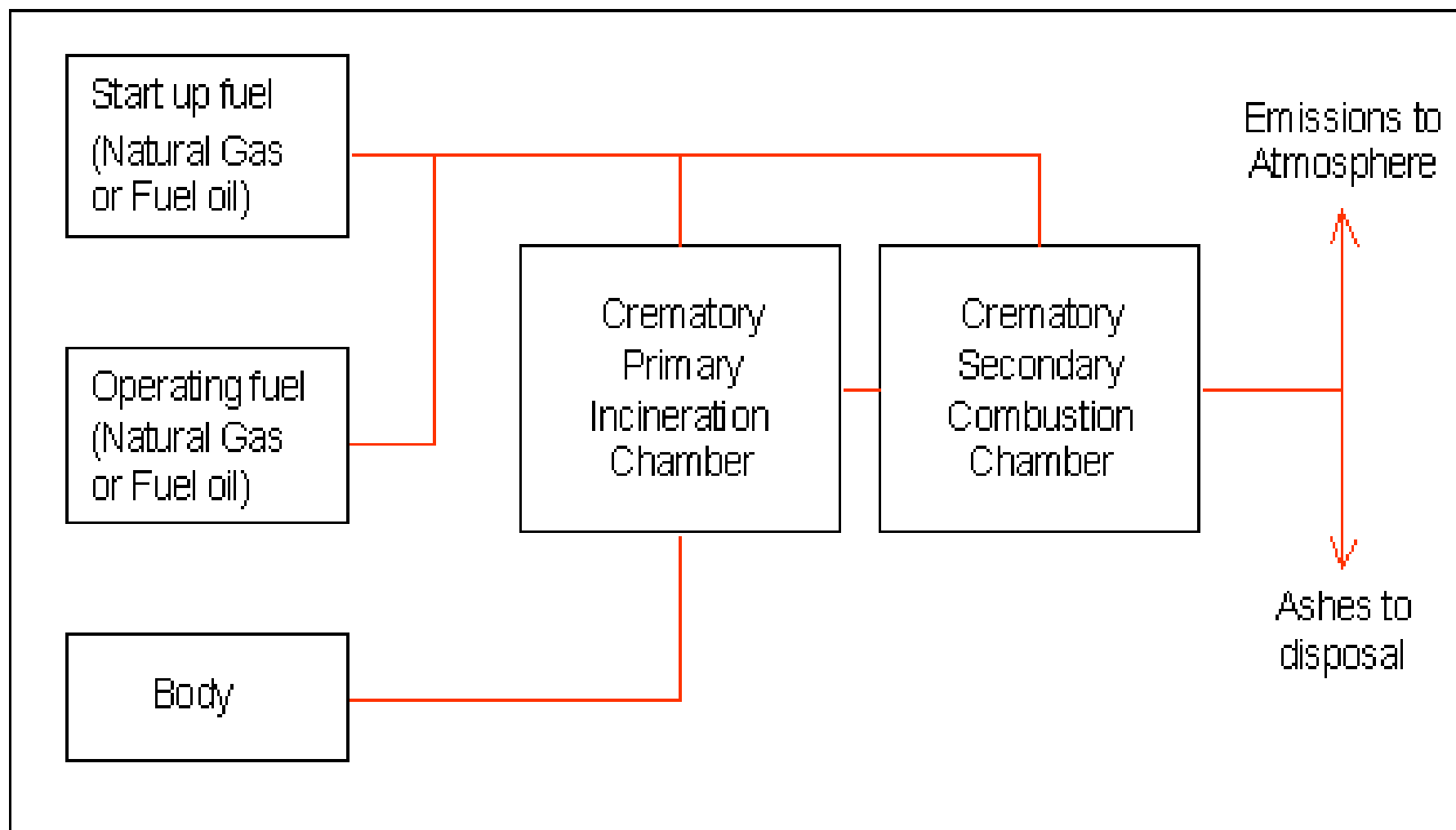
# Biomass/wood stoves

- ↪ **Replacing poorly designed stoves** with improved stoves that burn fuel more efficiently can be an effective strategy for reducing hazardous POPs releases and improving indoor air quality. In addition 50-80% of fuel may be saved
  
- ↪ **Options for effective use of improved stoves:**
  - ❖ Stove design should match the specific available fuel
  - ❖ Raising of public awareness about improved stoves
  - ❖ Training on appropriate use of stoves
  - ❖ Implement training programs for stove maintenance and repair
  - ❖ Cost-effectiveness of the new stoves
  - ❖ Raising of awareness about indoor air pollution and adverse health effects

# Crematoria

- ↪ **Purpose:** religiously and culturally accepted practice of dealing with the dead of human being; alternative to burial
- ↪ **BAT / BEP / BECT:** Avoidance of chlorinated materials, maintenance of efficient combustion conditions (T over 850 °C), residence time 2 seconds, sufficient air (> 6% O<sub>2</sub>), APC for sulphur dioxide, hydrogen chloride, CO, VOCs, dust and POPs (lime and activated carbon injection followed by a bag filter)
- ↪ **Performance:** dioxin/furan concentration < 0.1 ng TEQ.Nm<sup>-3</sup>

# Typical cremation process



# Motor vehicles burning leaded gasoline

- ↪ **Purpose:** Transportation by using gasoline and diesel as fuel; particularly leaded gasoline, where chlorinated and brominated scavengers are used
- ↪ **Alternatives:** use of other fuels, such as unleaded gasoline, diesel, LPG, CNG, propane-butane, bio-fuels and alcohol/oil mixtures
- ↪ **BAT/BACT:** banning of halogenated scavengers, fitting the vehicle with and oxidation catalyst or particulate filter



# Smoldering of copper cables

- ↪ **Purpose:** Recovering of scrap copper
  
- ↪ **BAT/BACT:** mechanical cable chopping, stripping or high temperature incineration ( $> 850\text{ }^{\circ}\text{C}$ ), residence time, excess oxygen, with APC
  
- ↪ **“Open burning is not an environmentally acceptable solution for any kind of waste” (UNEP 2001)**
  - ❖ Oxygen starved conditions
  - ❖ Low temperatures 250-700  $^{\circ}\text{C}$
  - ❖ Cu is catalyzing PCDD/PCDF formation

# Alternatives

- ↪ **Cable chopping**
  - ❖ Requires pre-sorting
  - ❖ Granulation (filtering is necessary)
  - ❖ Density/electrostatic separation (metal losses may occur)
- ↪ **Cable stripping**
  - ❖ Cheaper than chopping/lower throughput/lower cost
  - ❖ Presorting of the cables
  - ❖ Complete recovery
  - ❖ Rates: 60 m/min; 1.1 kg.min<sup>-1</sup>; cable diameter 1.6 mm-150 mm
- ↪ **High temperature incineration**
  - ❖ To treat cables unsuitable for stripping or chopping

# Specific chemical production processes

Most of the processes described share common steps, including:

- ↪ chlorination of organic or inorganic raw materials,
- ↪ purification of the products,
- ↪ separation of product streams (usually by distillation),
- ↪ destruction of high-molecular-weight side products and
- ↪ recycle or sale of hydrogen chloride.

# Specific chemical production processes

Efficient separation and destruction of chlorinated organic side products, which may include persistent organic pollutants, **is key to best available techniques applicable to these processes**, as is the associated guidance for any incorporated incineration processes.

For certain products, **modernized manufacturing processes** that reduce formation of persistent organic pollutants are also presented.

# Specific chemical production processes

**Crude products** of these reactions  $v$ , and as with virtually all industrial chemical processes, **are in overall yield and purities**, purification of the final product is **required prior to sale or further internal use**.

**Purification can involve separation** of a mixture of saleable products – in many cases a spectrum of useful products results from a single reaction treatment – or separation of saleable products from the inevitable formation of highmolecular-weight by-products.

For most organics and some inorganics that purification step involves **distillation**.

# Specific chemical production processes

Generally, high-molecular-weight by-products are not saleable as themselves.

In some cases they are thermally oxidized, with HCl, carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) as products of this oxidation.

**HCl is recovered and reused** as an integral part of the process.

In some cases they are viewed as wastes to be destroyed, usually by **hazardous waste combustion**, though HCl recycling is common.

# General process overview

**What the processes have in common:**

**HCl as coproduct; Need for purification**

**Organic,  
Inorganic  
Materials**

**Chlorine**

**Chemical  
Processes**

**Products**

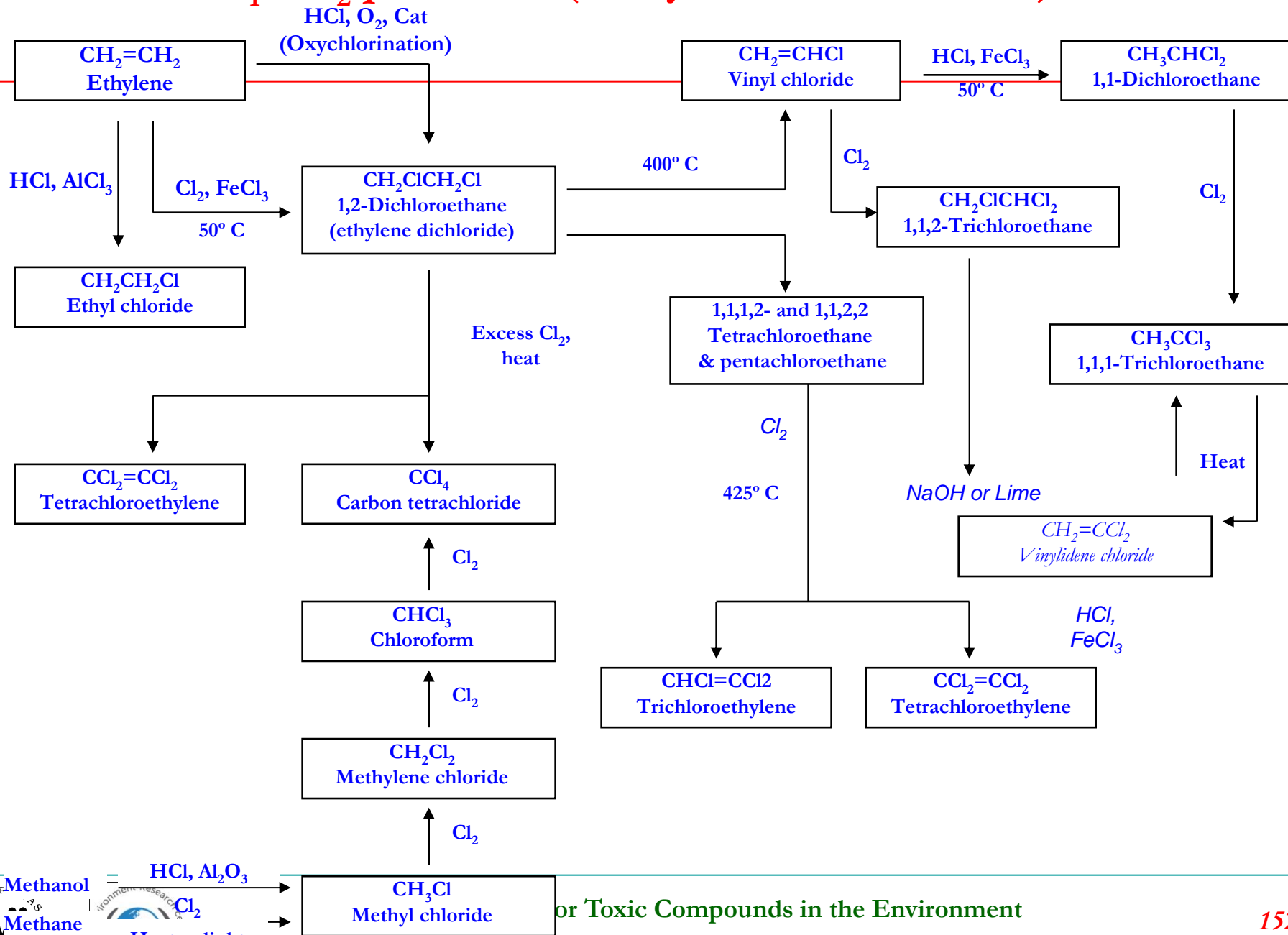
**By-  
Products**

**Co-Product  
HCl**

**Organics:** Allyl Chloride;  
Chloranil; Chloroprene;  
Chlorinated benzenes;  
Epichlorohydrin; Isocyanurates;  
Phosgene; Chlorophenols;  
Vinylidene Chloride; Vinyl  
Chloride, etc.

**Solvents:** Chloromethanes;  
Chlorinated Ethanes,  
Perchloroethylene;  
Trichloroethylene

# C<sub>1</sub> and C<sub>2</sub> processes (Wiley Interscience 2000)





# Co-product hydrogen chloride

**Hydrogen chloride (HCl)** is handled in one or more of the following ways:

- ↪ It can simply be neutralized and discharged as salt (sodium chloride).
- ↪ However, in some processes HCl can constitute a large amount of the effective use of input chlorine, so neutralization and discharge carries with it a large opportunity cost in the loss of potential raw material.

**HCl can be** recovered, hydrated and then sold as the commercial product muriatic (hydrochloric) acid or used for pH adjustment in chloralkali cells.

In the United States of America, muriatic acid - by-product of vinyl chloride production - about 20 pg I-TEQ l<sub>-1</sub> range (0.004 g I-TEQ/yr for United States commercial production)

Thus, there is some **recycling of HCl electrolytically** to chlorine.

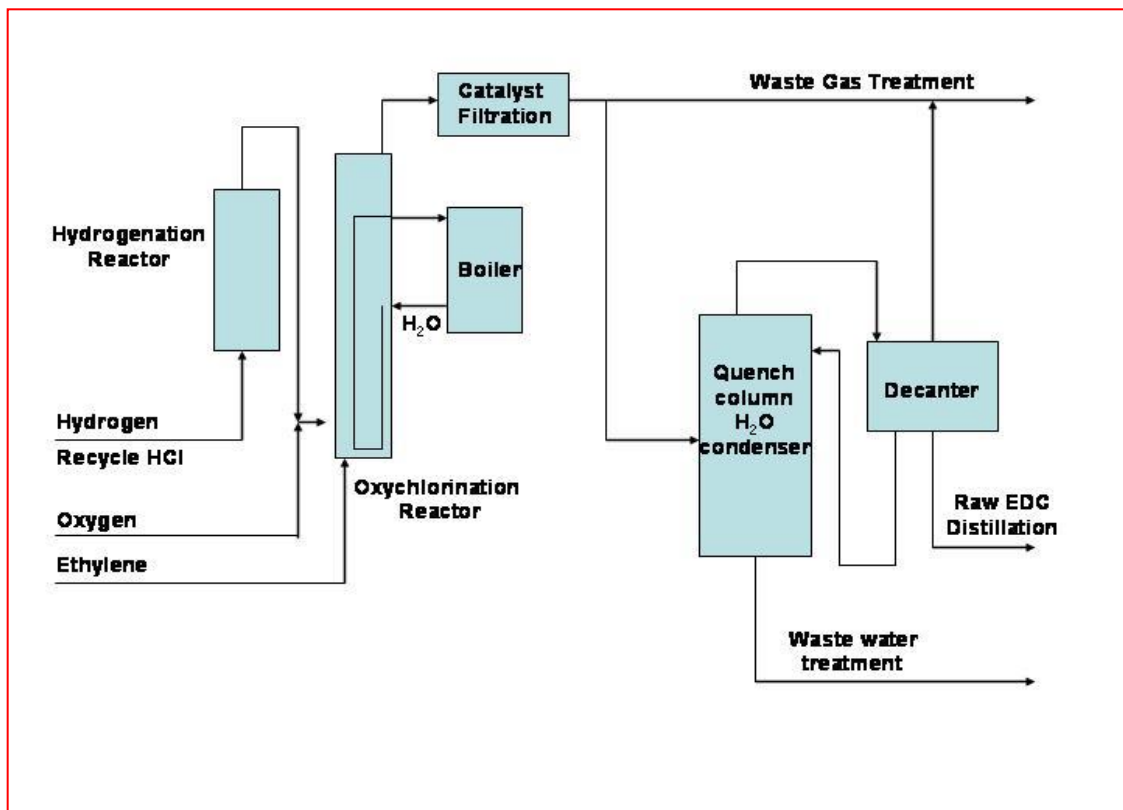
# Co-product hydrogen chloride

HCl can also be dried, oxidized catalytically and, in the presence of organic raw material, **reacted as elemental chlorine to generate** more of the desired product.

The process by which this is accomplished is called **oxychlorination** and constitutes a means of in process recovery of a valuable chlorine feedstock.

# Oxychlorination flow diagram

In oxychlorination, an organic such as ethylene reacts with dry HCl and either air or pure oxygen in a heterogeneous catalytic reaction. An example is the reaction involving HCl, oxygen and ethylene to form ethylene dichloride and water.



There are two types of catalyst systems used in oxychlorination: fixed bed and fluid bed.

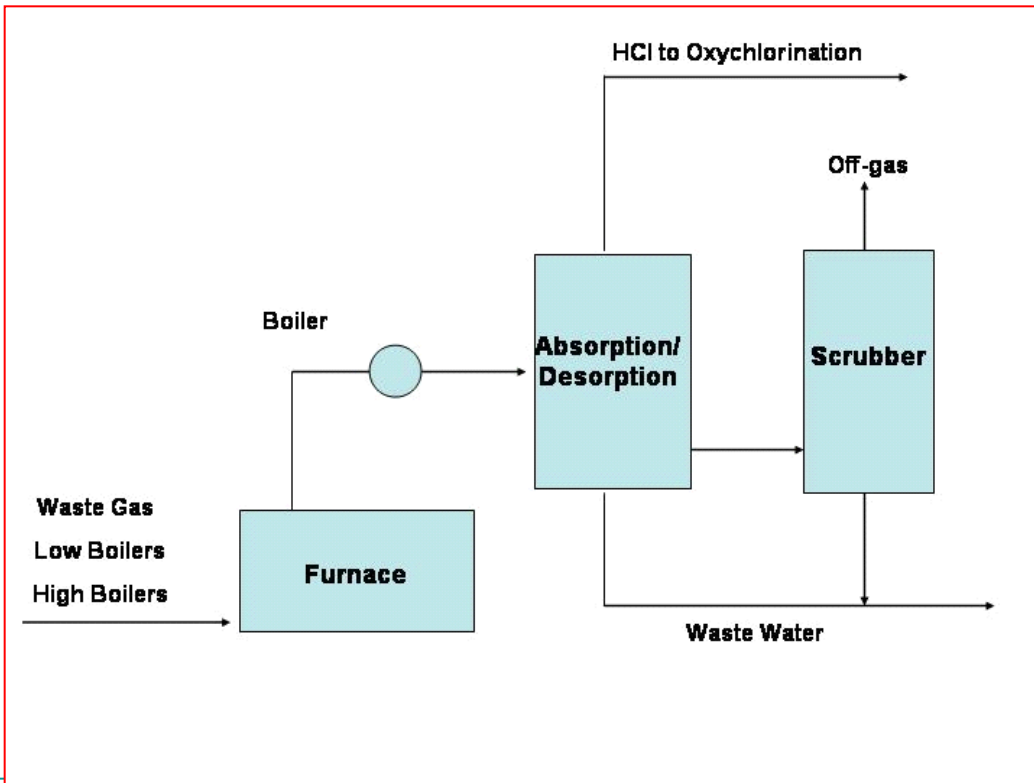
Both can be considered best available techniques (European Commission 2003).

Use of certain feedstocks in an oxychlorination process may lead to higher formation of persistent organic pollutants.

For example, oxychlorination of heavy ends on a vinyl chloride plant can give considerable yields of PCDD/PCDF (UK Environment Agency 1997).

# By product destruction

In general, best available techniques for airstreams can involve recovery and recycling of HCl, combustion of trace volatiles, scrubbing of incinerator output streams with water, alkaline solutions or dry alkali, and addition of activated carbon and baghouses for removal of particulate. These may be used alone or in combination.

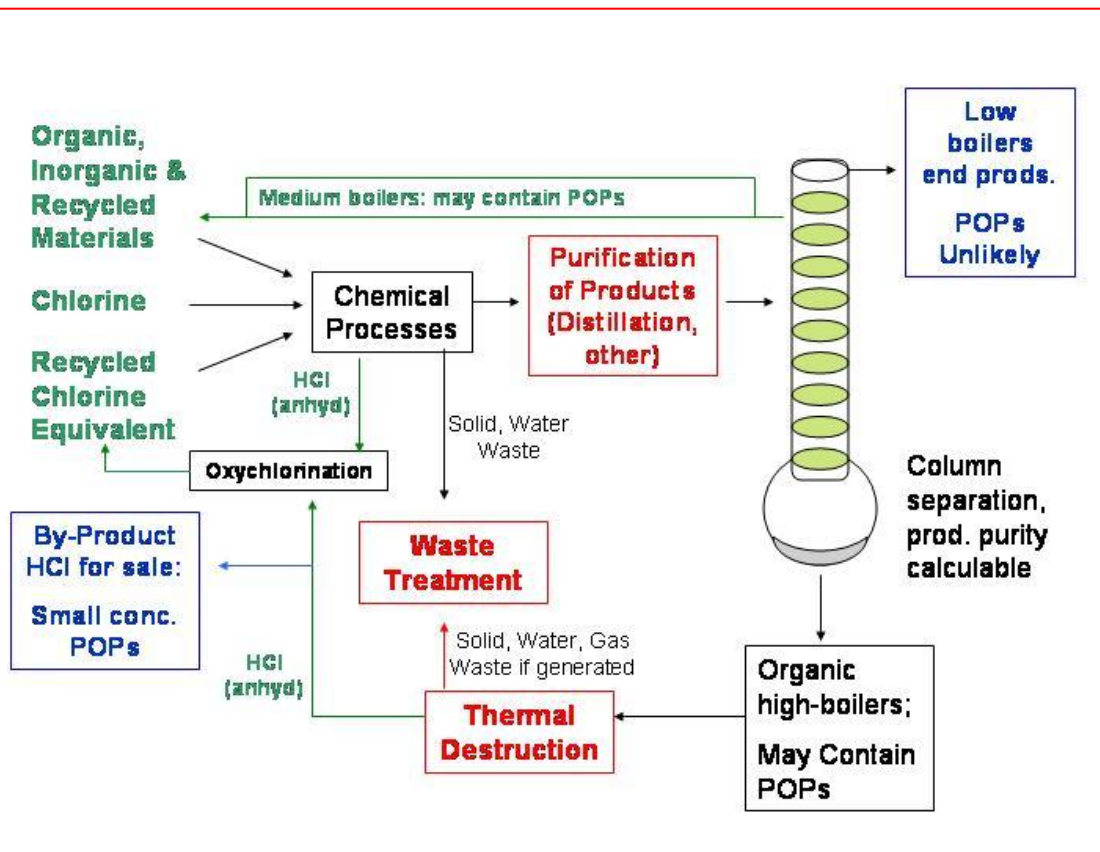


Treatment of water streams can involve stripping and recovery (condensation or absorption) of volatile materials from water. Subsequent biological purification of water streams with removal of solids is done in a dedicated water treatment system. Best available techniques for both streams will be considered in the granting of permits for facilities combusting heavy ends.

# Block diagram of generic organic process

Distillation is a standard engineering unit operation.

It is based on sequential vaporization and condensation of liquid in a column, which typically includes packing or trays in order to maximize its internal surface area. Vapour that reaches the top of the column is enriched in the lowest-boiling material present in the distillation mixture.



For non-azeotroping materials with widely separated boiling points – for example, vinyl chloride and PCDD/PCDF – virtually complete separations can be accomplished in a well-designed and operated column (ChEResources website).

# Mechanisms of formation of PCDDs/Fs in the manufacture of halogenated organic chemicals

US EPA (1997) - four major mechanisms have been postulated for the formation of halogenated dioxins and furans in the manufacture of halogenated organic chemicals:

- (1) direct halogenation of dioxins or furans...;
- (2) reaction of an ortho halogen with a phenate;
- (3) loss of the halogen (e.g., chlorine or bromine) from a halogenated phenate to form halogenated furans...;
- (4) reactions between ortho- and meta-substituted halogens”

Mechanism (1) assumes a preformed PCDD or PCDF ring structure, possibly unhalogenated.

Mechanisms 2–4 describe reactions of aromatic halides or halogenated phenols. A number of factors influence the amount of PCDD and PCDF that may be formed in a given manufacturing process, including temperature, pH, catalyst, and reaction kinetics (EPA 1997).

The influence of these factors may be modulated by the specific chemistry:or example, the presence of aromatic or aliphatic organic materials.

# Mechanisms of formation of PCDDs/Fs in the manufacture of halogenated organic chemicals

PCDD/PCDF generation in chemical processes to manufacture chlorine-containing materials generally decreases in the order (Fiedler et al., 2000) :

chlorophenols > chlorobenzenes > aliphatic chlorides > inorganic chlorides

This may also be modulated by other reaction conditions.

Total production will be affected both by propensity (ease) of formation and volume throughput so a large volume process such as chlorine production may give a larger mass flow than a highconcentration/higher-yielding but smaller-volume process.

# BAT/BEP in the chemical production

The main demands for modern and safe chemical production can be stated as:

- ↪ Application of best available techniques, including high-performance technologies, in the design and construction of installations
- ↪ Efficient closed cycles for the control of side products and destruction of wastes and emissions
- ↪ Effective management of side products and handling of wastes
- ↪ Dedicated facilities for destruction of wastes and emissions under the responsibility of the enterprise itself and with external control
- ↪ Commitment to a standard of  $0.1 \text{ ng I-TEQ m}^{-3}$  for air emissions in destruction of any side products, wastes and emissions
- ↪ Development of a clearly defined regime for internal and external monitoring of key operating parameters.



# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
Chlorine, caustic soda	$\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{NaOH} + \text{H}_2$	More common	
	See European Commission 2003a, 2003b; Expert Group presentation		
<b>Organics</b>			
Allyl chloride	Direct chlorination of propylene > 300° C	More common	HCl
	Pyrolysis of 1,2-dichloropropane	Less common	Chlorinated olefins, HCl

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>Organics</b>			
Chloranil dye	See UNEP 2003		
Chloroprene (2-chloro-1,3-butadiene)	$C_2H_2 + CuCl/NH_4Cl \rightarrow$ vinyl acetylene + HCl $\rightarrow$ chloroprene	Less common	
	Vapour phase: butadiene + Cl <sub>2</sub> $\rightarrow$ 1,4 & 3,4 dichloro; isomerized (Cu catalyst) to 3,4 dichloro; HCl via NaOH; distilled to separate low boiling mono-Cl <sub>s</sub> ; 3,4-di; 1,4-di; heavies	More common	NaCl; overchlorinated products

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>Organics</b>			
<b>Chlorinated benzenes</b>	Vapour phase: benzene + chlorine + HCl	Less common	Mixed product
	Liquid phase: Cl <sub>2</sub> /FeCl <sub>3</sub> to yield mix; controlled by amount of chlorinating agent (monos); some other specialized processes for certain isomers; high-Cl materials can precipitate. Purified by distillation and crystallization; separations difficult	More common	HCl

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>Organics</b>			
<b>Epichlorohydrin</b>	Allyl chloride + HOCl (chlorine water) → glycerol chlorohydrins + NaOH/(CaOH) <sub>2</sub> → epichlorohydrin	More common	Hydrolyzed product; polymers
	Steam stripped then distilled		
	Also: propylene + O <sub>2</sub> (Pd catalyst) → allyl acetate → allyl alcohol + Cl <sub>2</sub> → allyl chloride		

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>Organics</b>			
Isocyanurate disinfectants	Isocyanuric acid + NaOH + Cl <sub>2</sub>		
Phosgene	CO + Cl <sub>2</sub> used virtually immediately to produce polycarbonate and polyurethane		

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>Organics</b>			
<b>Chlorinated phenols</b>	Lesser chlorinated phenols; phenol + Cl <sub>2</sub> ; various Lewis acid catalysts; FeCl <sub>3</sub> , ZnCl <sub>2</sub>	More common	
<b>Pentachlorophenol (PCP)</b>	Phenol + Cl <sub>2</sub> ; AlCl <sub>3</sub> as main industrial catalyst; 100–180 °C	More common	HCl
	hexachlorobenzene (HCB) + NaOH	Less common	NaCl

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>Organics</b>			
Sodium pentachlorophenate	PCP + NaOH	More common	NaCl
	HCB + NaOH	Less common	NaCl
Vinylidene chloride (ViCl <sub>2</sub> )	1,1,2-trichloroethane + NaOH or Ca(OH) <sub>2</sub> ; can also be a co-product of high-temperature chlorination of C <sub>2</sub> materials	More common	NaCl or CaCl <sub>2</sub>

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>Organics</b>			
<b>Chlorinated phenols Pentachlorophenol (PCP)</b>	Lesser chlorinated phenols; phenol + Cl <sub>2</sub> ; various Lewis acid catalysts; FeCl <sub>3</sub> , ZnCl <sub>2</sub>	More common	HCl NaCl
	Phenol + Cl <sub>2</sub> ; AlCl <sub>3</sub> as main industrial catalyst; 100–180° C	More common	
	hexachlorobenzene (HCB) + NaOH	Less common	



# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>C<sub>1</sub> products</b>			
<b>Methyl chloride</b>	$\text{CH}_4 + \text{Cl}_2$ via heat or light	More common	
	$\text{CH}_3\text{OH} + \text{HCl} \rightarrow \text{CH}_3\text{Cl}$	More common	
<b>Other chlorinated methanes</b>	$\text{CH}_3\text{Cl} + \text{Cl}_2$ heat or light $\rightarrow$ $\text{CH}_2\text{Cl}_2, \text{CHCl}_3, \text{CCl}_4$	More common	
	$\text{CS}_2 + \text{Cl}_2 \rightarrow \text{S}_2\text{Cl}_2 + \text{CCl}_4$	Less common	
	$\text{CS}_2 + \text{S}_2\text{Cl}_2 \rightarrow \text{S} + \text{CCl}_4$		

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>C<sub>2</sub> products</b>			
<i>Chlorinated ethanes</i>			
1,1-di	VC + HCl/FeCl <sub>3</sub>	More common	
1,2-di (EDC)	Ethylene + Cl <sub>2</sub> → EDC (Fe cat) (direct chlorination)	More common	
	Ethylene + HCl + O <sub>2</sub> (Cu cat) → EDC (oxychlorination)		

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>C<sub>2</sub> products</b>			
<i>Chlorinated ethanes</i>			
<b>1,1,1-tri</b>	1,1-di + Cl <sub>2</sub> (photochemical)	More common	HCl
	1,1,2-tri → 1,1,1-tri	More common	
	Ethane + Cl <sub>2</sub>	Less common	
<b>1,1,2-tri</b>	VC + Cl <sub>2</sub>	More common	
	EDC + Cl <sub>2</sub>	More common	HCl

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>C<sub>2</sub> products</b>			
<i>Chlorinated ethanes</i>			
1,1,1,2-tetra, 1,1,2,2-tetra	EDC + Cl <sub>2</sub> (can include oxychlor)	More common	HCl
	C <sub>2</sub> H <sub>2</sub> + Cl <sub>2</sub>		
	C <sub>2</sub> H <sub>4</sub> + Cl <sub>2</sub>	More common	HCl
1,1,1,2,2-penta	TCE + Cl <sub>2</sub> → penta		

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>Chlorinated ethylenes</b>			
<b>Trichloroethylene (TCE) and perchloroethylene (PCE)</b>	$\text{EDC} + \text{Cl}_2 \rightarrow \text{TCE} + \text{PCE}$	More common	HCl
	$\text{EDC} + \text{Cl}_2 \rightarrow \text{PCE} + \text{CCl}_4$	More common	HCl
	$2 \text{CCl}_4 \rightarrow \text{PCE}$	More common	
	$\text{EDC} + \text{Cl}_2 + \text{O}_2 \rightarrow \text{PCE/TCE}$	More common	
	Tetrachloroethanes + heat $\rightarrow \text{TCE}$	More common	HCl
	Pentachloroethane + heat $\rightarrow \text{PCE}$	Less common	HCl

# Synthesis of commodity chemicals

Chemical	Process	Process use	Co-products
<b>Inorganics</b>			
HCl	By-product; salt + sulphuric acid; hydrogen + chlorine; recovery from combustion of chlorinated organics	More common	
TiO <sub>2</sub>	C, Cl <sub>2</sub> , TiO <sub>2</sub> ore → TiCl <sub>4</sub> + O <sub>2</sub> → TiO <sub>2</sub>	More common	Cl <sub>2</sub> , recycle
	TiO <sub>2</sub> ore + H <sub>2</sub> SO <sub>4</sub> → Ti(SO <sub>4</sub> ) <sub>2</sub> → TiO <sub>2</sub>	Less common	sulphates
FeCl <sub>3</sub>	Iron or iron oxide + HCl → FeCl <sub>3</sub>		
Hypochlorites	Na: 2NaOH + Cl <sub>2</sub> → NaOCl		NaCl
	Ca: Ca(OH) <sub>2</sub> + 2Cl <sub>2</sub> → Ca(OCl) <sub>2</sub> also via NaOCl used as aid in chloride removal; recovered, then dried		CaCl <sub>2</sub>
ZnCl <sub>2</sub>	Zn + HCl → ZnCl <sub>2</sub>		
ClO <sub>2</sub>	Generated from HClO <sub>2</sub> or NaClO <sub>3</sub>		

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

Contamination with PCDD and PCDF has been found in both textile and leather products.

The occurrence of PCDD/PCDF in the textile and leather industries is due to use of chlorinated chemicals, especially pentachlorophenol and chloronitrofen, to protect the raw material (e.g. cotton, wool or other fibres, leather); and use of dioxin contaminated dyestuffs (e.g. dioxazines or phthalocyanines).

Smaller quantities of PCDD/PCDF may be formed during finishing, and during incineration of process generated sludges.

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

Alternatives to the above-listed dye pigments exist and those listed should not be applied.

Possible alternatives to pentachlorophenol and chloronitrofen include 2-(thiocyanomethylthio) benzothiazole (TCMTB); o-phenylphenol (oPP); 4-chloro-3-methylphenol (CMK); and 2-n-octyl-4-isothiazolin-3-one (OIT).

As regards best available techniques, the most efficient primary measure to prevent contamination of textiles and leather goods with PCDD/PCDF would be not to use dioxin-contaminated biocides and dyestuffs in the production chains.



# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

Also, if any of the above-mentioned chemicals are being used, preference should be given to batches containing low concentration (e.g. distilled or otherwise purified chemicals).

To the extent possible, burning of textile, upholstery, leather products and carpet should be avoided to prevent PCDD/PCDF formation.

In order to prevent or minimize formation and release of PCDD/PCDF when burning sludge from wastewater treatment and flotation using the best available techniques for industrial boilers.

However, other environmentally sound techniques should also be explored.

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

The textile industry exhibits one of the most complicated manufacturing chains.

It is a fragmented and heterogeneous sector dominated by small and medium-sized enterprises; for example, in 2000 in the European Union, 114 000 companies employed about 2.2 million people (European Commission 2003b).

Demand is largely driven by three main end uses: clothing, home furnishing and industrial use.

The textile and clothing chain is composed of a wide number of subsectors covering the entire production cycle from the production of raw materials (artificial fibres) to semiprocessed products (yarns, woven and knitted fabrics with their finishing processes) and final or consumer products (carpets, home textiles, clothing and industrial use textiles).

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

## Process description

**Woven and knit fabrics** cannot be processed into finished goods until the fabrics have passed through several water-intensive wet processing stages (also known as finishing) such as fabric preparation, dyeing, printing and finishing.

**Natural fibres typically require more processing steps** than artificial fibres.

**Relatively large volumes of wastewater** are generated, containing a wide range of contaminants, which must be treated prior to disposal.

**Significant quantities of energy** are used in heating and cooling chemical baths and drying fabrics and yarns.

Fabric preparation requires desizing, scouring and bleaching as well as singeing and mercerizing.

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

Dyeing operations are used at various stages of production to add colour and intricacy to textiles and increase product value.

Dyes used by the textile industry are largely synthetic.

Finishing encompasses chemical or mechanical treatments (EPA 1997).

The main environmental concerns in the textile industry are the amounts of water discharged and the chemical load it carries.

Other important issues are energy consumption, air emissions, solid wastes and odours.

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

Although there is a multitude of steps in the production chain and environmental concerns do occur, generation of PCDDs/Fs could not be associated to individual production steps.

Instead, more attention has to be given to the facts that PCDDs/PCDFs enter the textile production process through application of pesticides and dyestuffs contaminated with PCDDs/PCDFs and that the PCDDs/PCDFs contamination is being carried through the various steps of the production chain.

Depending on the individual steps, solvents applied and the physical environment, PCDDs/PCDFs either stay in the textile product or are discharged as wastes.

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

Sources of chemicals listed in Annex C of the Stockholm Convention

In the textile production chain, the finishing processes are typically not sources of PCDDs/Fs formation (Horstmann et al. 1993).

Rather, the use of PCDDs/Fs containing dyes and pigments and the use in some countries of PCDDs/Fs contaminated fungicides to treat unfinished raw materials such as cotton appear to be the sources of the detected PCDDs/Fs.

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

New formation of PCDDs/Fs may occur in the textile production chain where effluents are treated and sludge is being removed and incinerated.

Such plants typically are considered to be modern.

Thus, measures that constitute **best available techniques and best environmental practices** will focus on:

- ↪ PCDDs/Fs contamination through introduction of dioxin-contaminated chemicals into the textile production chain;
- ↪ **New formation of PCDDs/Fs** in thermal disposal operations of production specific wastes.

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

So far, there are no reports on PCDDs/Fs contamination at or around leather plants.

However, contamination of commercial leather products has been reported and, based on the PCDDs/Fs pattern, it can be assumed that principally the processes identified in the textile industry are also responsible for the occurrence of PCDDs/Fs in leather products and in emissions (UNEP 2003).

The primary source of contamination seems to be pentachlorophenol.

This assumption is underlined by the fact that since its ban in Germany in 1989 the PCDDs/Fs concentrations in leather goods have declined (European Commission 1996).



# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

Best available techniques and best environmental practices

General good management practices include staff education and training, maintenance of equipment (and its documentation), chemical storage, handling, dosing and dispensing, and improved knowledge of inputs and outputs of the processes.

Knowledge about the textile raw materials is essential in managing pollution transfers.

Raw wool fibres may be contaminated with pesticides, sometimes organochlorine pesticides, including pentachlorophenol and chloronitrofen.

Effective washing and wool scouring, for example with perchloroethylene, will effectively remove all grease and pesticides that are typically found in the solvent phase.

For artisanal activities, responsible authorities should advocate improvement in basic housekeeping and occupational safety. Information and awareness programmes should be undertaken.

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

## Alternatives

Since the occurrence of PCDDs/Fs in the textile and leather industries is primarily linked to the use of dioxin-contaminated chemicals such as pentachlorophenol and certain dye pigments, substitution of these chemicals by dioxin-free chemicals would be the alternative.

For example, in Germany after the **phase-out of pentachlorophenol as a preservative**, the following chemicals have been used:

- ↙ 2-(thiocyanomethylthio) benzothiazole (TCMTB; CAS Registry No. 21564-17-0)
- ↙ o-phenylphenol (oPP; CAS Registry No. 90-43-7)
- ↙ 4-chloro-3-methylphenol (CMK; CAS Registry No. 59-50-7)
- ↙ 2-n-octyl-4-isothiazolin-3-one (OIT; CAS Registry No. 26530-26-1)

# Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)

The above-mentioned chemicals are assessed as **less hazardous for the environment than pentachlorophenol** but they are not inherently safe at all.

Safer alternative chemicals should be explored.

As much as possible, it is **imperative to avoid burning textile, upholstery, leather products and carpet** to prevent PCDDs/Fs formation.

# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

The main processes involved in making pulp and paper products are raw material handling and preparation, storage (and preservation for non-woods), wood debarking, chipping and agricultural residue cleaning, deknottling, pulping, pulp processing and bleaching if required and, finally, paper or paperboard manufacturing.

Of the 17 PCDD/PCDF congeners with chlorine in the 2,3,7 and 8 positions, only two congeners – namely 2,3,7,8-TCDD and 2,3,7,8-TCDF – have been identified as potentially being produced during chemical pulp bleaching using chlorine.

Most of the formation of the 2,3,7,8-TCDD and 2,3,7,8-TCDF is generated in the C-stage of bleaching via the reaction of chlorine with precursors of TCDD and TCDF. HCB and PCB are not formed during pulp bleaching.

# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

As a summary, the following primary measures can be taken for decreasing or eliminating the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in wood and non-wood bleaching processes:

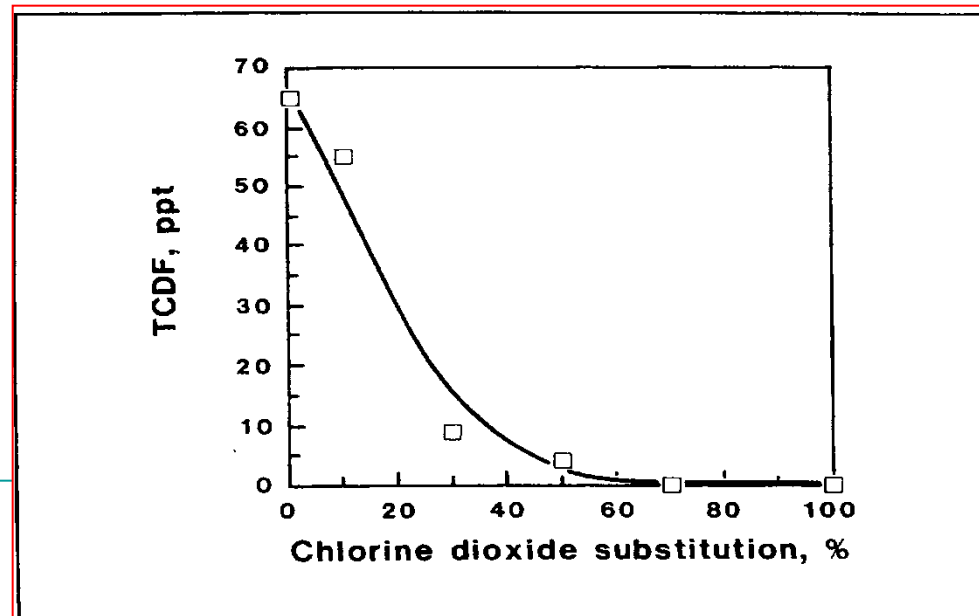
- ↙ eliminate elemental chlorine by replacing it with chlorine dioxide (elemental chlorine-free bleaching) or in some cases with totally chlorine-free processes;
- ↙ reduce application of elemental chlorine by decreasing chlorine multiple or increasing the substitution of chlorine dioxide for molecular chlorine;
- ↙ minimize precursors such as PCDDs/Fs entering the bleach plant by using precursor-free additives and thorough washing;
- ↙ maximize knot removal; and
- ↙ eliminate pulping of furnish contaminated with polychlorinated phenols.

# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

The intense international research showed that the principle mechanism for formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF is the chlorination of the precursor compounds dibenzodioxin (DBD) and dibenzofuran (DBF) present in the unbleached pulp via aromatic electrophilic substitution.

The formation of 2,3,7,8-TCDF will be reduced by increasing chlorine dioxide substitution, as shown in Figure.

The use of molecular chlorine in bleaching has been largely replaced by chlorine dioxide (ECF, elemental chlorine-free) and other oxygen-based chemicals such as molecular oxide, peroxide and ozone (TCF, totally chlorine-free).



# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

## Raw materials

Pulp and paper are manufactured from **wood-based materials** and from many kinds of **non-wood materials**, such as straw, bagasse, bamboo, reeds and kenaf.

At present, **wood provides over 90% of the world's** virgin fibre requirement while non-wood sources provide the remainder.

**In 2005**, the production of wood-based chemical pulps was about 126 million tons and the production of non-woods 17 million tons.

Non-wood pulps are mainly produced in developing countries, but for many reasons non-wood pulp fibres are gaining new interest in Eastern and Western Europe as well as in North America (Paavilainen 1998).

# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

Wood and the main non-wood materials used in papermaking represent a complex mixture of the same substances:

- ↙ Cellulose (40–45%)
- ↙ Hemicelluloses (25–35%)
- ↙ Lignin (20–30%)
- ↙ Extractives (2–15%)

Most ligno-cellulosic and cellulosic materials of **fibrous structure** may be processed into various grades of papers and paperboard.

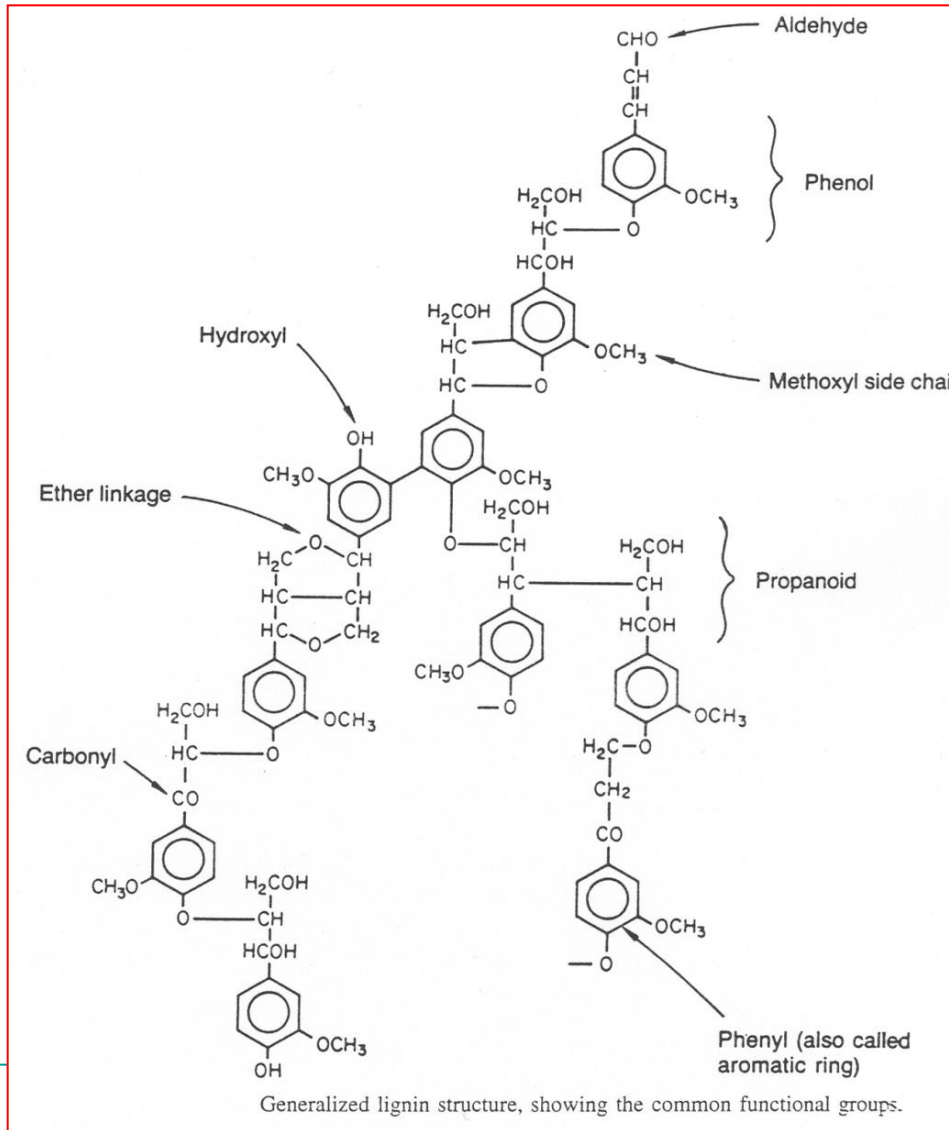
Fibres from different raw materials are, however, dissimilar.

They differ considerably in their morphological and chemical characteristics, which make them suitable for varying grades of final products (Paavilainen 1998).



# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

## Lignin



# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

## Technology and final product

**Pulping and bleaching technology** must be matched with the quality and characteristics of the pulp and paper grades to be produced.

No single pulping or bleaching process can produce pulp suitable for all uses.

For instance, **newsprint is a high-volume product** of moderate strength, opacity and printability, and it has a relatively short life.

Therefore, a high yield of pulp at the expense of maximum achievable strength and brightness can be manufactured from the raw materials, and there is a lower bleaching requirement due to the natural brightness of the pulps.

# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

Process description - Pulping methods applied

The main processes involved in making pulp and paper products are raw material handling and preparation, storage (and preservation for non-woods), wood debarking, chipping and agricultural residue cleaning, deknottling, pulping, pulp processing and bleaching if required and, finally, paper or paperboard manufacturing.

The manufacture of pulp utilizes mechanical, thermomechanical, chemimechanical and chemical methods.

Lignin binds the fibres in the wood structure - in chemical pulping, the release of fibres is facilitated by chemicals that dissolve lignin.

# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

The lignin and many other organic substances are thus put into solution.

This occurs in pressure vessels, called digesters, which are heated, pressurized vertical stationary vessels for wood-based raw material.

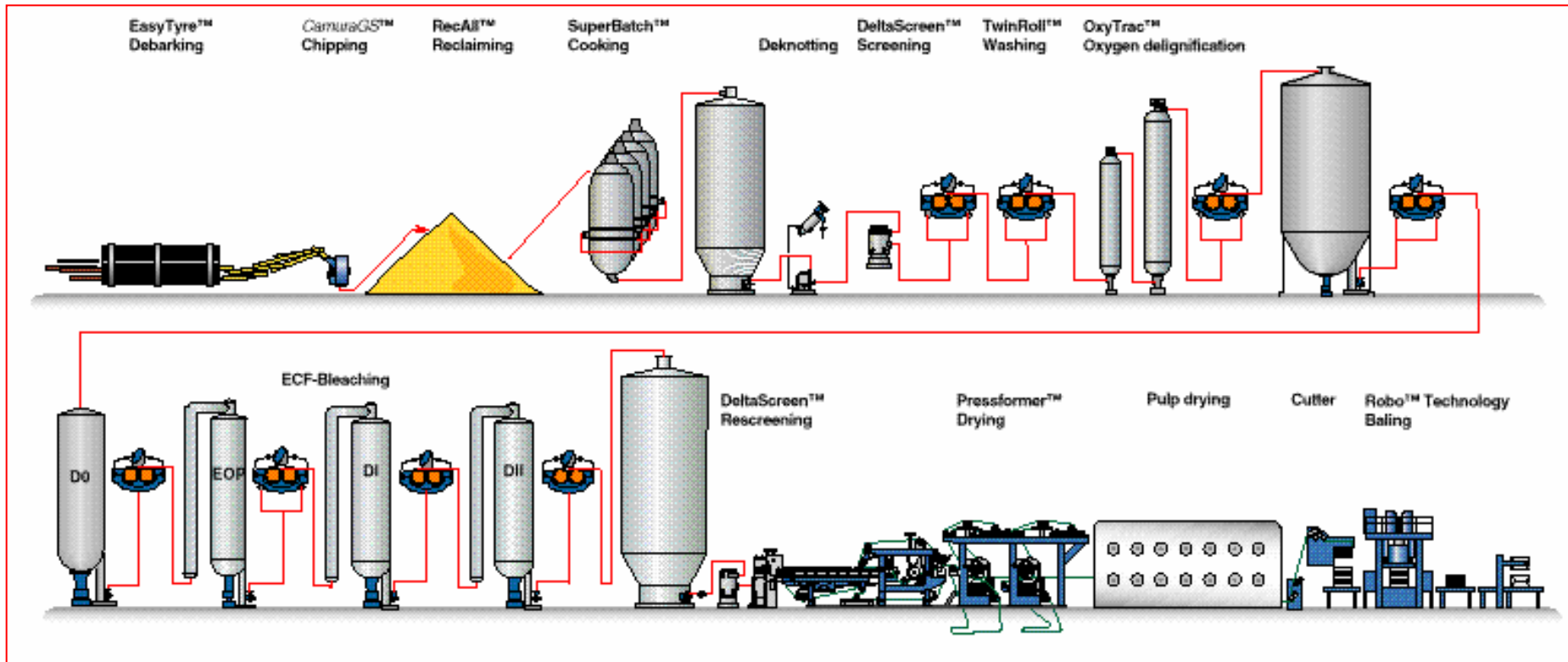
Spherical rotary digesters or tumbling cylindrical digesters are used in batch pulping systems in various chemical processes for non-woods.

# Production of pulp using elemental chlorine or chemicals generating elemental chlorine

The main chemical, semi-chemical and chemimechanical pulping techniques are as follows:

- ↙ Sulphate (kraft) uses a mixture of sodium hydroxide and sodium sulphide under alkaline conditions to dissolve the lignin from wood and most non-wood fibres (chemical method);
- ↙ Sulphite: Acid bisulphite, bisulphite, alkaline and neutral sulphite methods (Ca, Mg, NH<sub>4</sub>, Na); different bases, including anthraquinone, under a range of pH, to dissolve the lignin; most wood fibres (chemical and semi-chemical methods);
- ↙ Lime, lime-soda: In particular, non-wood fibres;
- ↙ Cold soda uses sodium hydroxide pretreatment at ambient temperatures, alone or with sodium carbonate: In particular, hardwood and non-wood fibres (semichemical);
- ↙ Soda anthraquinone (AQ): Sodium hydroxide alone or with sodium carbonate and a catalyst anthraquinone; hardwood and non-wood fibres (chemical, similar to kraft but without sulphur), reduced odour;
- ↙ Organosolv methods: Wood and non-wood applications, some proven at mill scale but only one process is available commercially.

# Typical flow diagram for modern Kraft pulping process with ECF-bleaching. Courtesy of Metso Automation Inc.



**The kraft or sulphate process** is the dominating pulping process worldwide, constituting 84% of the world's chemical pulp production and 63% of total chemical and mechanical pulp production.

# Pulp bleaching

**Bleaching after pulping** is a chemical process applied to pulps in order to increase their brightness.

**To reach the required brightness** level, bleaching should be performed by removing the residual lignin of chemical pulps (delignifying or lignin-removing bleaching).

**All lignin cannot be removed** selectively enough in a single bleaching stage, but pulp is usually bleached in three to six stages.

**The first two stages** primarily release and extract lignin, and the subsequent stages **remove the lignin residues and finish the product.**

These bleaching sequences are applied to maximize the bleaching effect of each component.

Water is used to perform intermediate washes to remove extracted waste from the pulp.

# Pulp bleaching

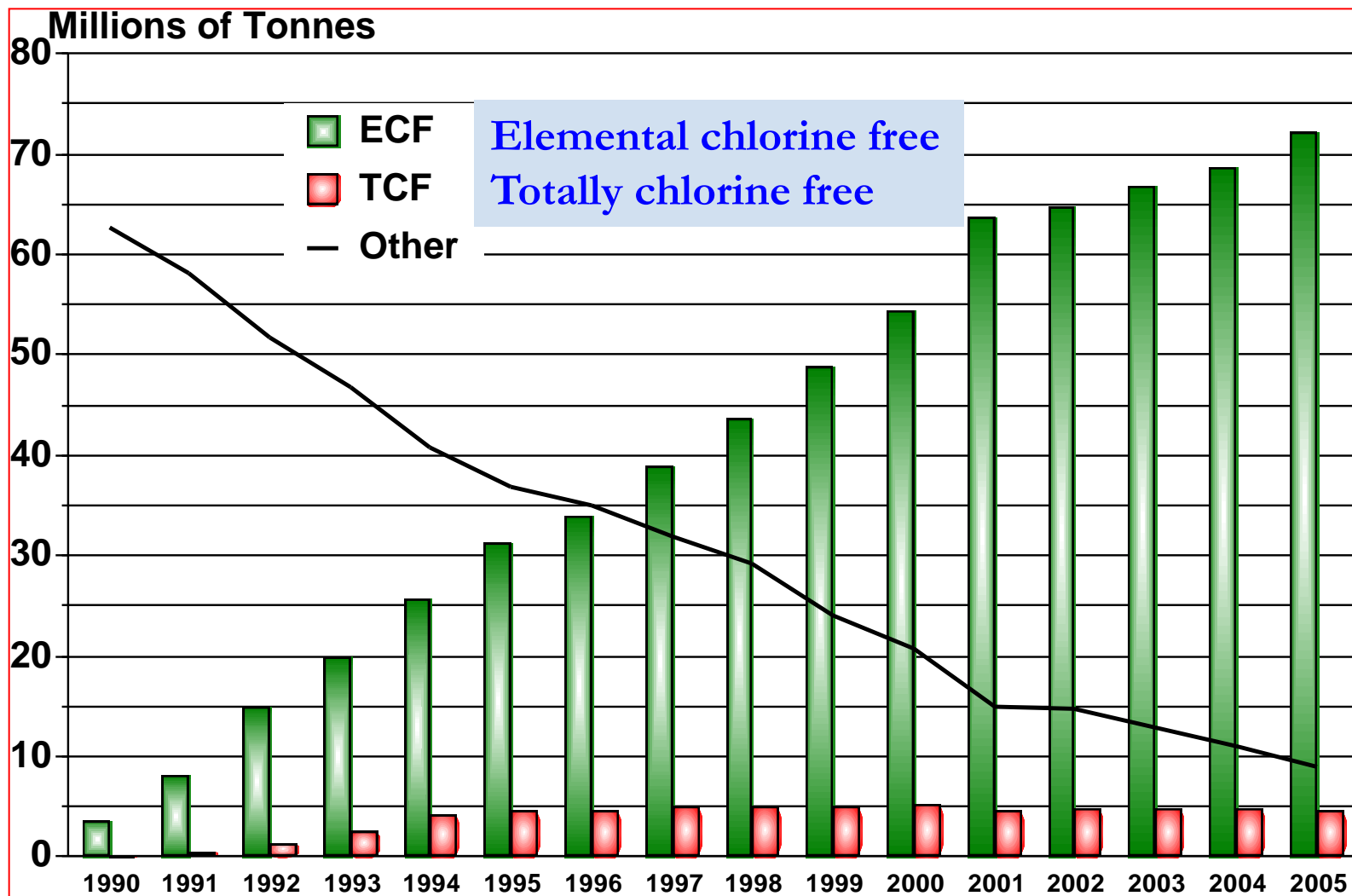
Treatment	Abbreviation	Description
Chlorination	C	Reaction with elemental chlorine in acidic medium
Alkaline extraction	E	Dissolution of reaction products with NaOH
Hypochlorite	H	Reaction with hypochlorite in alkaline medium
Chlorine dioxide	D	Reaction with chlorine dioxide ( $\text{ClO}_2$ )
Chlorine and chlorine dioxide	CD	Chlorine dioxide is added in chlorine stage
Oxygen	O	Reaction with molecular oxygen at high pressure in alkaline medium
Extraction with oxygen	EO	Alkaline extraction with oxygen
Peroxide	P	Reaction with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in alkaline medium
Chelating	Q	Reaction with chelating agent EDTA or DTPA in acidic medium for removal of metals
Ozone	Z	Ozone using gaseous ozone ( $\text{O}_3$ )

1960s and 1970s - CEHDED nebo CEDED

Now - CD(EOP)D, OD(EOP)DP, Q(PO)DD, (Z(EO)DD



# Trends in bleached chemical pulp production (world excluding China and India)



Research Centre for Toxic Compounds in the Environment

<http://recetox.muni.cz>

# Best available techniques for production of pulp using elemental chlorine

## Primary measures

The principal best available techniques for minimizing or eliminating the formation of 2,3,7,8-TCDD/TCDF in wood and non-wood bleaching processes are as follows:

- ↙ **Reduction of the application of elemental chlorine** by decreasing the multiple or increasing the substitution of  $\text{ClO}_2$  for molecular chlorine;
- ↙ **Elimination of elemental chlorine** by replacing it with  $\text{ClO}_2$  (elemental chlorine free bleaching) or with chlorine-free chemicals;
- ↙ **Utilization of DBD-** and **DBF-free** defoamers;
- ↙ **Prevention of using non-wood raw material** (reeds) that are contaminated or potentially contaminated by PCDD/PCDF as impurities in sodium pentachlorophenolate (Zheng 1997)
- ↙ **Effective brownstock washing** to enable the reduction of chlorine multiple;
- ↙ **Maximization of knot and dirt removal** to enable the reduction of chlorine multiple;
- ↙ **Elimination of the pulping of furnish** contaminated with polychlorinated phenols.

# Best available techniques for production of pulp using elemental chlorine

## Secondary measures

### The following general measures are suggested:

- ↙ **Substitution:** The identification and substitution of potentially harmful substances with less harmful alternatives. Use of a detailed inventory of raw materials used, chemical composition, quantities, fate and environmental impact;
- ↙ **Investment planning/cycles:** Coordination of process improvements to reduce technical bottleneck delays in the introduction of better techniques;
- ↙ **Training, education and motivation of personnel:** Training staff can be a very cost-effective way of reducing discharges of harmful substances;
- ↙ **Process control monitoring and optimization:** To be able to reduce different pollutants simultaneously and to maintain low releases, improved process control using elemental chlorine or chemicals generating elemental chlorine is required, including raw materials specification and monitoring of raw materials for precursor materials;

# Best available techniques for production of pulp using elemental chlorine

- ↪ **Process control monitoring and optimization:** To be able to reduce different pollutants simultaneously and to maintain low releases, improved process control using elemental chlorine or chemicals generating elemental chlorine is required, including raw materials specification and monitoring of raw materials for precursor materials;
- ↪ **Adequate maintenance:** To maintain the efficiency of the process and the associated abatement techniques at a high level, sufficient maintenance has to be ensured;
- ↪ **Environmental management system:** A system that clearly defines the responsibilities for environmentally relevant aspects in a mill. It raises awareness and includes goals and measures, process and job instructions, checklists and other relevant documentation, and incorporation of environmental issues into process change controls;
- ↪ **Development of environmental monitoring and standard monitoring protocols,** including release monitoring for new facilities.

# PCDDs/Fs – requirement for continuing minimization and, where feasible, ultimate elimination, by

- ↪ Establishing an action plan (within 2 years);
- ↪ Establishing and maintaining release inventories;
- ↪ Promote/require use of substitute or modified materials, products and processes to prevent the formation and release of unintentional POPs;
- ↪ Application of best available techniques (BAT) and best environmental practices (BEP);
- ↪ For new priority sources: as soon as possible but not later than 4 years after entry-into-force.

# Disposal of POPs waste

Wastes and stockpiles have to 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.

# Disposal of POPs waste

For the member states of the European Union the Council Directive 96/59/EG allows only four disposal operations for PCB-containing wastes:

- ↪ biological treatment
- ↪ physico-chemical treatment
- ↪ incineration on land
- ↪ permanent storage (only in safe, deep, underground storage in dry rock formations and only for equipment containing PCBs and used PCBs which cannot be decontaminated)

# Disposal of capacitors

- ↪ The small capacitors are a problematic group because they are a diffuse source of PCBs if they are not removed from the devices before their disposal.
- ↪ Furthermore, PCB-containing capacitors cause the formation of polychlorinated dioxins and furans if they are mixed with ordinary municipal waste and incinerated together with it.
- ↪ PCB-containing and PCB-suspicious small capacitors have to be removed from the equipment and to be deposited of in an underground landfill.



# Disposal of transformers

**Large transformers** may have an overall-mass of several tons from which the mass of the fluid may be more than one ton.

If the metals of the transformer – iron from the core-plates and copper from the coils – shall be recycled, the transformers must be emptied and the metals have to be cleaned from PCBs.

Only PCB-free metallic parts may be recycled in thermal metallurgical processes without emissions of polychlorinated dioxins and furans.

There are available systems of solvent-washing of equipment which has been removed from service.

# LTR<sup>2</sup> (Low Temperature Rinsing and Re-use) system of ABB

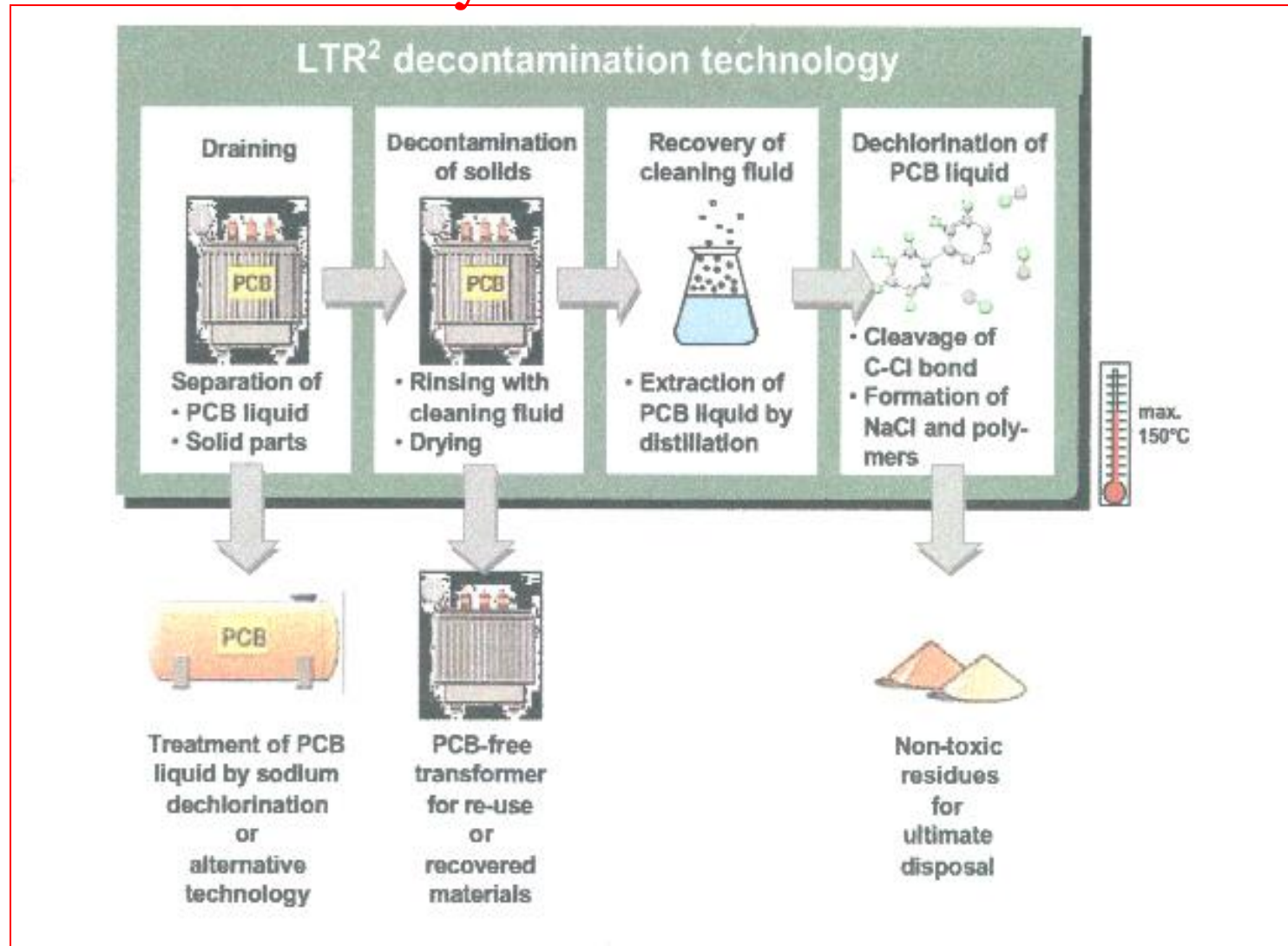
Marries ABB's experience in transformer maintenance and recycling (used commercially for more than 15 years on over 30 000 transformers to date) with Sodium Reduction (NaR) technology.

Principally for PCBs and mineral oils contaminated with PCBs.

## Principal advantages:

- ↪ factors-in costs for new or recycled equipment for the equipment owner
- ↪ operates at low temperatures and pressures minimising attendance risks and input costs
- ↪ works with low-contaminated transformers in situ
- ↪ uses an effective solvent (tetrachloroethylene) to rinse PCBs from highly contaminated transformers
- ↪ relatively mobile and scalable

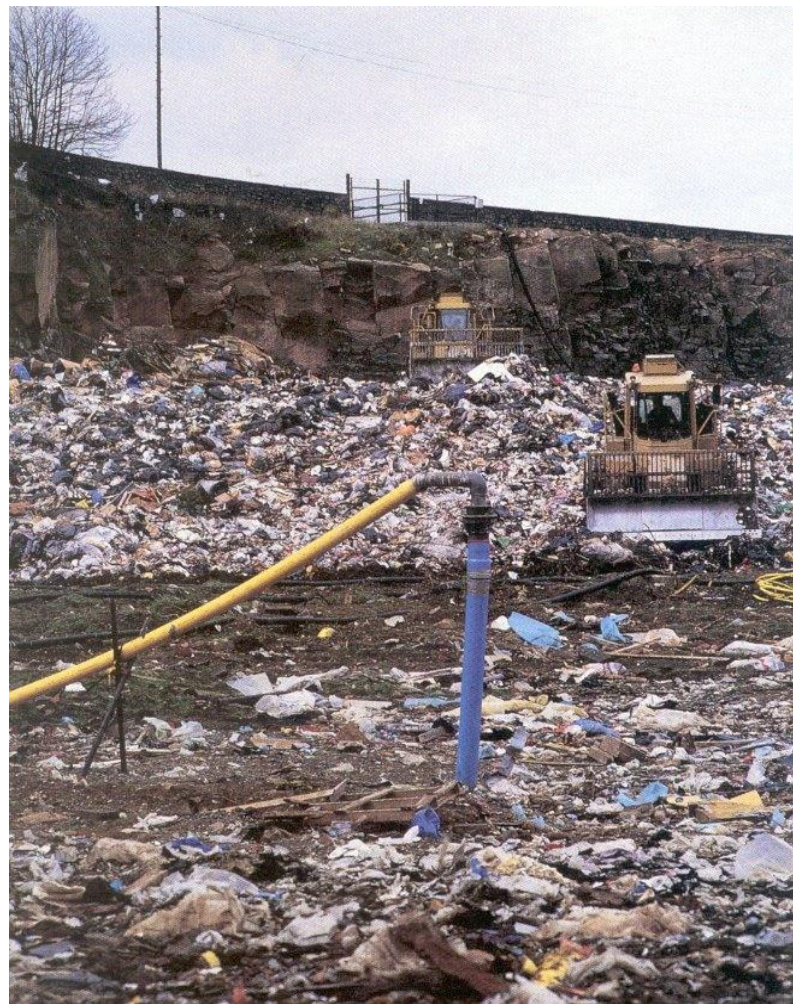
# LTR<sup>2</sup> (Low Temperature Rinsing and Re-use) system of ABB



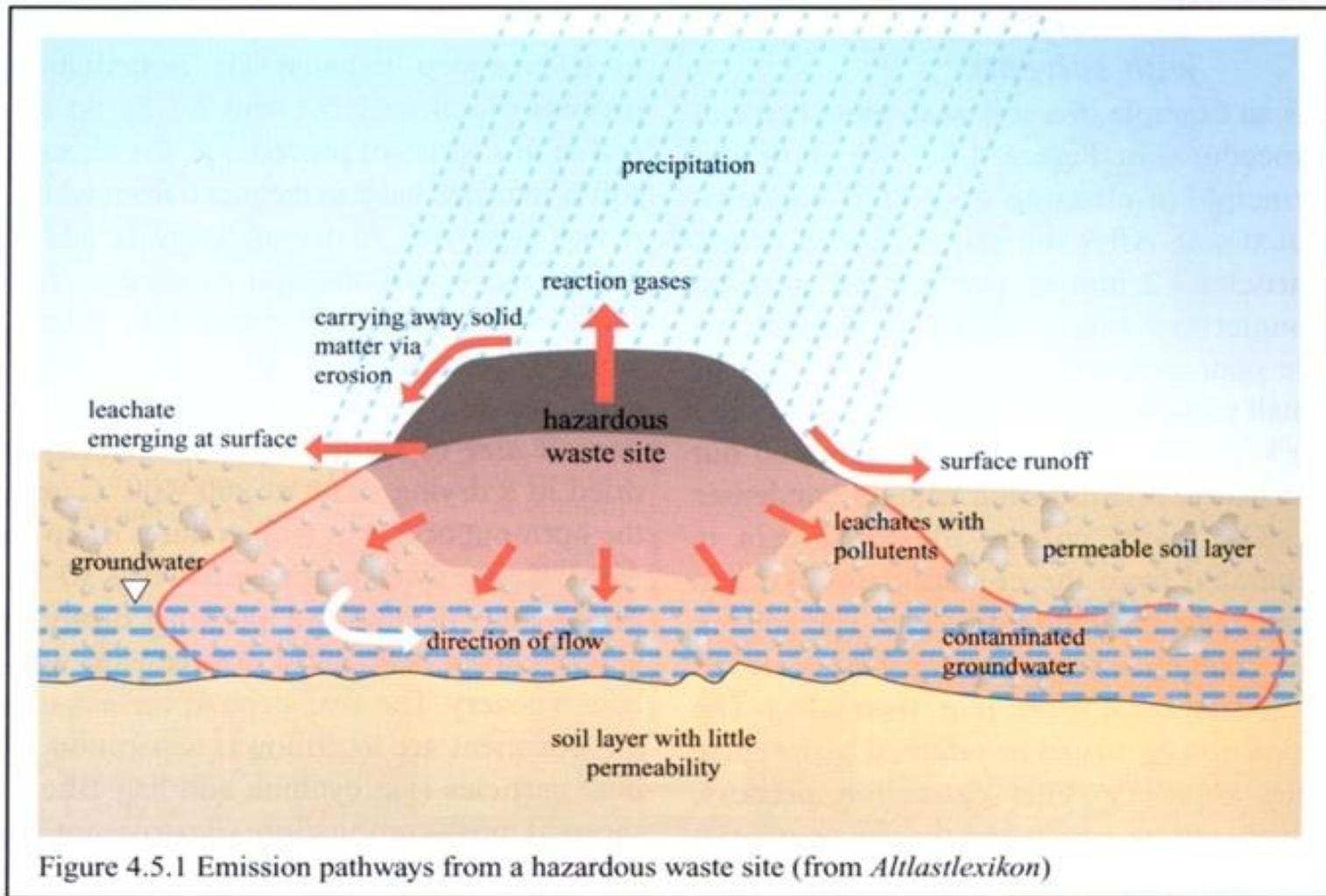
# Disposal of transformers

- ↪ Because of the internal structure of transformers its complete cleaning is not an easy process.
- ↪ It may be cheaper not to recycle the metals but to dispose them of in an environmental sound manner.
- ↪ In these cases the transformers are emptied, rinsed and filled up with a binder, are geometrically conditioned and, like small capacitors, deposited in an underground landfill.
- ↪ This procedure fulfils the demand of the European Directive mentioned above in the sense of a “permanent storage” far from the biosphere.

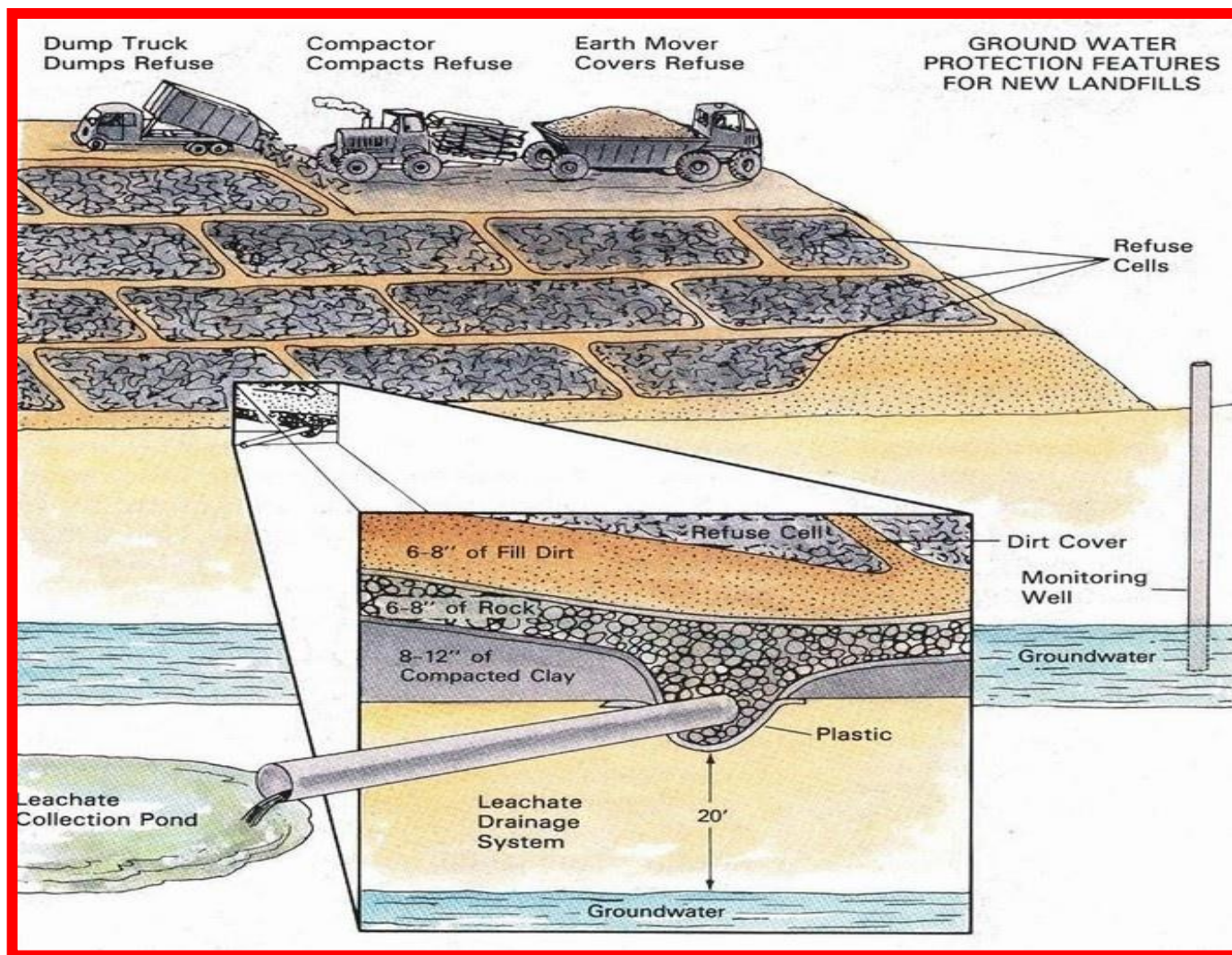
# The worst case of POPs wastes management – disposal on dumping sites



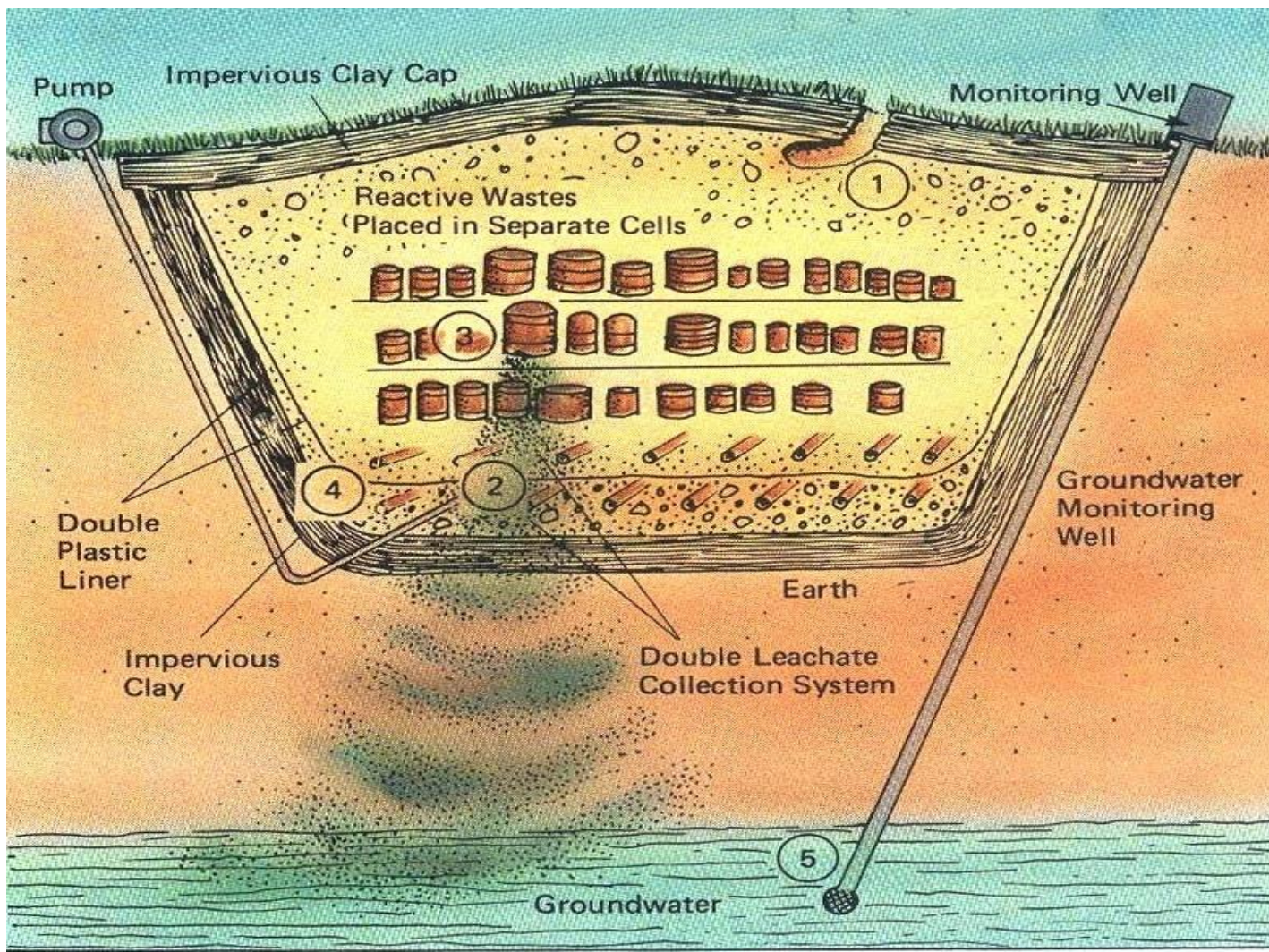
# Hazardous waste site - emission pathways



# Groundwater protection - hazardous waste site



# Hazardous waste site





# Best environmental practise – best storage practise



Research Centre for Toxic Compounds

<http://recetox.muni.cz>

# Best environmental practise – best storage practise



- ↪ Solution of POPs waste problems to the moment when we will have generally acceptable technics for destruction
- ↪ Economically more acceptable in present time than any development and construction of new facility (combustion/non-combustion)

# Underground landfills

- ↪ **Underground landfills** in for example in Germany are former salt mines or separated parts of still existing mines.
- ↪ **They are situated several 100 m under the earth's surface and isolated from ground water and the biosphere by natural sealants, e.g. clay layers.**
- ↪ **They are organized like warehouses with separated areas for, e.g., mercury containing wastes, arsenic containing wastes and PCB-containing wastes.**
- ↪ **Within a limited period of time the wastes deposited in an underground landfill may be moved back if necessary.**
- ↪ **After a longer time (several hundred years) the salt flows around the wastes, wrapping them – for eternity.**

# Underground landfills

- ↪ **Underground landfilling/underground waste stowing as a non-destructive method of treating wastes containing POPs is now a highly recognized form of treatment, especially for wastes which are not thermally treated due to economical and ecological reasons, for example filter dust from waste incineration plants.**
- ↪ **This method of disposal as laid out in the Stockholm Convention should therefore be allowed use in the future.**
- ↪ **The amounts disposed of in Germany are from domestic as well as foreign origin.**
- ↪ **Dioxin contaminated filter dust, especially from waste incineration but also from metallurgic processing, make up the greater part of the wastes.**
- ↪ **Whilst the PCDD/F concentrations in filter dust from waste incineration amount to less than 10 000 ng.kg<sup>-1</sup>, filter dust from metallurgic processing in some cases significantly exceed this amount (rising up to 100 000 ng.kg<sup>-1</sup>).**

# Biological treatment

- ↪ **The biological treatment, however, is a slow process and not well suited for the detoxification of wastes containing PCBs.**
- ↪ **Biological methods are under development and applied in the remediation of contaminated areas, especially in cases when an off-site treatment is not possible.**

# UNEP Resources



## PCB Inventory Form

First issue  
August 2002

### Inventory of PCB-Containing Equipment

Record number:	
Date:	
Inspector:	

A	Information about the company and the site		
1	Name:		
2	Address:		
3	Address of site: (if different from A2)		
4	Phone:		
	Fax:		
	E-mail:		
5	Name/position of contact:		
6	Type of company / Industry type / production at specific site:		
7	Public or private company?		
8	Location:	Industrial zone Other urban area Rural area	
	9	Number of staff at visited site:	>50 10-50 <10
		10	Total number of pieces of equipment at site
11			Total electricity consumption at site
	12		PCB elimination action plan in place? - action plan intended but not started? - previous disposal activities? - time frame for program?



United Nations  
Environment Programme



## PCB Transformers and Capacitors

### From Management to Reclassification and Disposal

First Issue  
May 2002



PREPARED BY UNEP CHEMICALS

IOMC

INTERNATIONAL PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS  
A cooperative agreement among UNEP, ILO, FAO, WHO, UNCTAD, UNCTAW and OECD

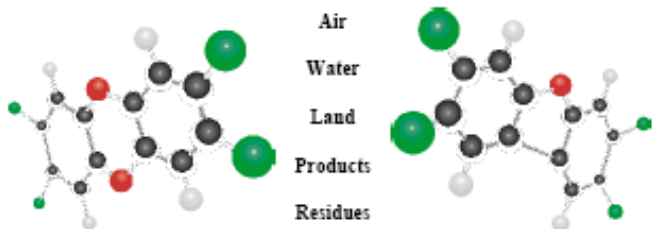
# UNEP Resources



UNITED NATIONS  
ENVIRONMENT PROGRAMME



## Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases



1<sup>st</sup> edition  
May 2003

Prepared by UNEP Chemicals  
Geneva, Switzerland

IOMC

INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS  
A cooperative agreement among UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD



United Nations  
Environment Programme



## Asia Toolkit Project on Inventories of Dioxin and Furan Releases National PCDD/PCDF Inventories



Prepared by  
UNEP Chemicals, Geneva

July 2003

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INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS  
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