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## MINI-BREF 3

# INSTALLATIONS FOR THE PHYSICO-CHEMICAL TREATMENT

[extract from *BREF for the Waste Treatments Industries* from August 2006]

Note: Text in blue corresponds to references also mentioned in MINI-BREF 1-Common techniques

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## 2. General information

Introduction / purpose / scope / wastes treated by Ph-C plants ...

### 1.1. Installation for the treatment of waste

#### Installations for the physico-chemical treatment of waste waters

This sector is represented by a large range of processes which are classed as 'chemical treatments'. These range from blending systems with no actual chemical interactions to complex plants with a range of treatment options, some custom designed for specific waste streams.

The process is designed to treat waste waters (contaminated with, e.g acid/alkalis, metals, salts, sludges), but usually accepts a range of organic materials as well, e.g. process plant washings and rinsings, residues from the oil/water separation, cleaning wastes, interceptor wastes, etc. These could contain almost any industrial material. It is likely that the treatment process will have some effect on the organic materials, for example due to some chemical oxidation of COD, some organics could be adsorbed or entrained in the sludge or, in emulsion treatment, part of the organic content could become separated from the aqueous phase.

These treatment systems remove and/or detoxify hazardous constituents dissolved or suspended in water. The selection and sequence of unit processes will be determined by the characteristics of the incoming wastes and the required effluent quality. An example of a physico-chemical treatment facility of waste waters typically contains the following unit processes: cyanide destruction, chromium reduction, two-stage metal precipitation, pH adjustment (e.g. neutralisation), solid filtration, biological treatment, carbon adsorption, sludge dewatering, coagulation/flocculation and some others.

Country	Number of known installations		Known capacity (kt/yr)	
	Hazardous	Non-hazardous	Hazardous	Non-hazardous
Belgium	8	Y		
Denmark	4	Y		
Germany	249	9000		
Greece	0	0	0	0
Spain	49		901	
France	19	Y	301	
Ireland	4	Y		
Italy	147	Y		
Luxembourg	1	0		0
Netherlands	30	0		0
Austria	33	Y	515	
Portugal	2	Y	22000 m <sup>3</sup>	
Finland	36	0 <sup>1</sup>	144	0
United Kingdom	32	289		
Iceland	0	0	0	0
Norway	4	Y		
<b>TOTAL</b>	<b>618</b>	<b>9289</b>	<b>1883</b>	
Y: exists but no data are available <sup>1</sup> No non-hazardous installations with this operation only Note: Numbers within this table may not reflect the real number of installations or capacity. The main reasons are that the market is so dynamic that numbers change rapidly and/or because no data have been provided by the TWG at all on certain topics. Cells without numbers mean that no information has been provided.				

**Table 2.1: Installations for the physico-chemical treatment of waste**  
 [60, Azkona and Tsotsos, 2000], [61, Weibenbach, 2001], [86, TWG, 2003], [150, TWG, 2004]

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The physico-chemical (Ph-c) treatment of waste water typically divides the waste into another type of waste (typically solid) and an aqueous effluent which is not usually considered waste as it is part of another legislation.

Ph-c plants are essential to medium and small companies including commercial enterprises. Waste which must be treated by Ph-c plants will, in future, continue to be produced (in the course of production); obligatory acceptance of waste by generally accessible Ph-c plants is an advantage for trade and industry, facilitating correct disposal of waste and easing the economic burden for industry and trade.

The following principal configurations can be identified:

- company in-house Ph-c plants. These are specialised for the treatment of the waste produced by a company
- generally accessible Ph-c plants (service plants). These are suitable for the treatment of waste produced in certain regions.

### **Installations for the treatment of combustion ashes and flue-gas cleaning residues**

During combustion processes, solid waste may be generated. Such solid waste is typically called 'ashes'. Two types are usually present; one called 'bottom ash', typically recovered at the bottom of the combustion chamber and another called 'fly ash' that is smaller and flows with the combustion fumes. This latter one is usually recovered with flue-gas cleaning equipment. Such flue-gas cleaning equipment is not only applicable to fly ash but also to extract from the other pollutants flue-gases. In doing so, different types of waste can be generated. This section contains those installations that treat such a variety of waste generated during combustion processes as well as other flue-gas cleaning processes.

Combustion ashes and flue-gas cleaning residues are one of the main waste stream treated by stabilisation and solidification processes, either in the combustion plant (e.g. in some incinerators), or on waste treatment facilities. Other methods are vitrification, purification and recycling of some components (e.g. salts). Another method of treating combustion ashes involves the fusion of ash by plasma at very high temperatures in order to vitrify the structure. One installation exists in France with a total treatment capacity of 3.5 kt per year.

### **Installations for the treatment of waste contaminated with PCBs**

Incineration, when available, is the most widely available and used technology for PCB destruction. The complete destruction of PCB by incineration only takes place under well defined conditions (e.g. high temperature and a higher residence time). Because of the cost of incineration, however, and its non-availability in many countries, alternative technologies are sometimes used.

### **Installations for the treatment of contaminated refractory ceramics**

Two installations are in operation in France with a total treatment capacity of 50 kt per year.

## **1.2. economic and institutionnel aspects of waste treatment sector**

### **Physico-chemical (Ph-c) treatment plants**

There are continuous changes in the production process modifying the type of waste as well as the auxiliary substances used. In this respect, even the Ph-c plants are subject to constant adaptation processes, both in terms of the procedures used and the controls. Furthermore, changes in the regulatory frameworks also lead to plant reconfigurations; in general, these changed regulations aim at a significant reduction in Ph-c plant emissions. The

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reconfiguration can affect all the functional areas of a Ph-c plant, including plant technology, process materials, laboratory equipment, and even the general and specialist knowledge of the staff.

### **1.3. General environmental issues related to installations that treat waste**

Air emissions / waste outputs / water emissions

NON OFFICIAL FEAD VERSION

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## 2. Applied processes and techniques

### Physico-chemical treatments of waste

[30, Eklund, et al., 1997], [51, Inertec, et al., 2002], [53, LaGrega, et al., 1994], [55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [89, Germany, 2003], [100, UNEP, 2000], [101, Greenpeace, 1998], [121, Schmidt and Institute for environmental and waste management, 2002], [123, Perseo, 2003], [124, Iswa, 2003], [136, Straetmans, 2003], [146, Galambos and McCann, 2003], [150, TWG, 2004], [152, TWG, 2004], [156, VROM, 2004], [157, UBA, 2004].

This section details the physico-chemical (Ph-c) treatments of waste. Treatments such as precipitation, decanting and centrifuging, and thermal treatments not included in WI BREF are included here. Due to the fact that many of these treatments are common unit operations, the description of some operations will only be mentioned briefly in this section. For those techniques considered less common and that need extra explanations, an independent section within this section has been created. Techniques for the abatement of emissions are covered in Section 2.6. Common activities carried out in these plants (e.g. storage, handling) are covered in Section 2.1.

The structure of this section relates to the physical conditions of the type of waste. Treatments carried out on liquids and solids differ a lot and it has been suggested that considering these separately may give a good structure to such a long section. At the end of the section, some special physico-chemical treatments carried out on special wastes (e.g. destruction of POPs) have also been included.

Some of the techniques for the treatment of waste may make use, for example, of the acidic solution from the first scrubber in a wet air pollution control system when air pollution control waste treatment is being considered. Some techniques involve a return of the treated residues to the combustion chamber for sintering with bottom ash. These techniques are not included in this document because they are integrated measures of the combustion technologies. These issues can be found in other BREF documents.

### 2.1. Physico-chemical treatments of waste waters

#### Purpose

Ph-c plants are planned in such a manner that the maximum amount of recyclable materials can be separated so that a minimum amount of auxiliary materials is used. The purposes of physico-chemical treatment plants are to:

- enable delivery of environmental protection goals, in particular, water quality management. In Ph-c plants, materials which may be hazardous to water are either treated, withheld and/or converted to a non-hazardous form
- enable the correct disposal of large quantities of, in general, aqueous liquid waste and waste requiring special controls
- separate the oil or the organic fraction to be used as fuel.

The procedures serve the specific application of physico-chemical reactions for material conversion (e.g. neutralisation, oxidation, reduction) and for material separation (e.g. filtration, sedimentation, distillation, ion exchange).

#### Principle of operation

During the physico-chemical treatment of contaminated waste water, water is separated and processed for discharge to sewerage systems or water bodies. This processed water becomes subject to various water legislation as soon as it is discharged.

#### Feed and output streams

The waste treated in Ph-c plants is aqueous liquid. Ph-c plants generally treat waste liquids or sludges with a relatively high water content (>80 w/w-%). Regardless of their origin and their relationship to their material characteristics, the wastes commonly treated by these plants are:

- emulsions/cooling lubricants
- acids (e.g. picking acids from surface treatments. Some information on STM BREF)
- alkaline solutions
- concentrates/saline solutions containing metals
- wash-water
- waste water containing a gasoline/oil separator
- solvent mixtures
- sludges
- aqueous liquid wastes with high concentrations of biodegradable materials
- aqueous marine waste.

An indication of the type of wastes accepted at sites in the UK is given in Table 2.1.

Waste stream	Percentage of sites accepting each type of waste (%)
Neutral aqueous inorganics	69
Acids	62
Oils	62
Alkalis	54
Neutral aqueous organics	54
Contaminated containers	23
Cyanides	23
Organic sludges	8
Water reactive chemicals	8

**Table 2.1: Waste types accepted at physico-chemical treatment plants in the UK [56, Babbie Group Ltd, 2002]**

#### Process description

Ph-c plants are configured on a case-by-case basis depending on requirements and/or application. Each Ph-c plant has a specific individual technological and operational concept; this is geared to the waste to be treated. For this reason, there is no 'standard' physico-chemical treatment plant. Although all plants have inspection and process laboratories and tend to have a neutralisation function, the range of pretreatment processes, sludge handling methods and the combination of input waste streams makes each a unique operation. The modes of operation of Ph-c plants are:

- continuous operation: particularly suitable for large throughputs, waste of relatively constant composition and for automated operation
- batch operation: particularly well suited to the very variable characteristics/reaction of the waste to be treated.

Table 2.2 shows some differences between different Ph-c plants.

	Treatment of
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	emulsions	emulsions and oil/water mixtures	emulsions and waste with contents to be detoxicated	liquid and aqueous waste with some organic solvents	liquid and aqueous waste containing organic solvents and tensides
Sieving					
Sedimentation					
Ultrafiltration					
Evaporation					
Heating up					
Stripping					
Acid splitting					
Organic splitting					
Oxidation/reduction					
Membrane filtration					
Flocculation/precipitation					
Sedimentation					
Draining					
Sulphuric precipitation					
Filtration					
Ion exchanger					
Neutralisation					

Note: Dark grey: required process, light grey: Optional process

**Table 2.2: Analysis of some representative types of physico-chemical treatment plants**  
Based on [121, Schmidt and Institute for environmental and waste management, 2002]

The unit operations typically used are sieving, storage/accumulation, neutralisation, sedimentation, precipitation/flocculation, ion exchange, oxidation/reduction, sorption (adsorption/absorption), evaporation/distillation, membrane filtration, stripping, extraction, filtration/draining, acid splitting of emulsions and the organic splitting of emulsions.

Frequently several unit operations will have to be used to correctly treat a specific waste. The unit operations procedure combination (type of procedure, sequence of their application, controls) is specified by the Ph-c plant laboratory, on the basis of the composition of the waste and its reaction behaviour.

The following equipment is typically available for reactors in order to control reactions:

- storage vessels for separate storage, depending on the type of treatment
- reaction containers with adjustable agitators and temperature indicators
- sedimentation containers
- metering equipment
- receiver and storage tanks for chemicals
- storage tanks and reservoirs for the waste to be treated
- dosing equipment
- material resistant to acids and alkalis
- control of pH value for the chemicals
- containers for settling and mixing ancillary agents
- measurement and automatic controls
- ventilation and filtering of the reaction tanks with facilities for cleaning the exhaust air.

**Users**

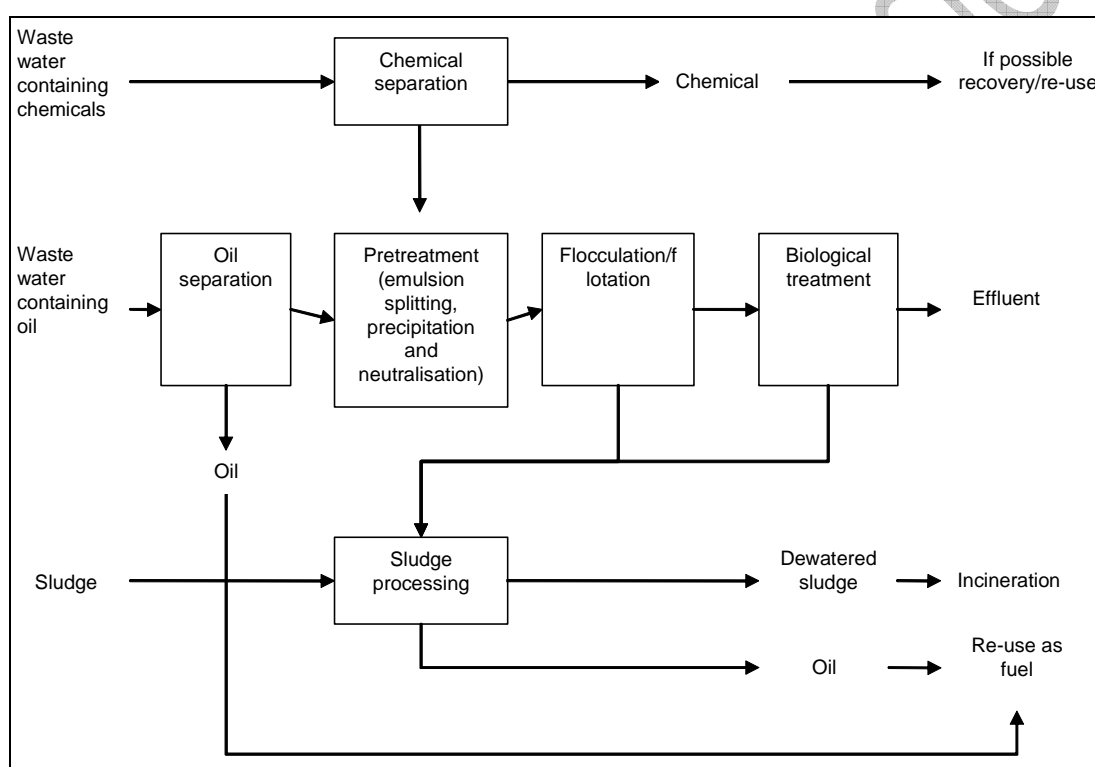


From 25 to 30 % of all hazardous waste in Germany is disposed of by Ph-c plants. Some examples of the operations carried out via a Ph-c plant are:

- treatment of emulsions
- treatment of emulsions and waste with contents to be detoxified
- treatment of liquids, aqueous wastes with some organic solvents
- treatment of emulsions and oil/water mixtures
- treatment of liquids, aqueous wastes containing organic solvents and tensides
- detoxification (oxidation/reduction) of waste containing nitrites, Cr(VI), cyanide (as pretreatment).

The wastes processed are usually from various industrial and commercial production processes, and from maintenance, repair and cleaning activities. Some specific industrial sectors served are the printing and photographic industries. These are an example of those sites, which provide a service to a particular industrial sector, taking away a wide range of wastes and transferring those that cannot be treated or recycled in-house.

Figure 2.1 shows the treatment of aqueous marine waste.



**Figure 2.1: Treatment of aqueous marine waste**  
[156, VROM, 2004]

## 2.2. Unit operations used in Ph-c treatments of waste waters

Waste can be treated using any of a large number of commercially proven unit operations. The treatment methods fall into four categories:

- phase separation (e.g. sedimentation, steam stripping)
- component separation (e.g. ion exchange, electrodialysis)
- chemical transformation (e.g. chemical oxidation, incineration)
- biological transformation (e.g. fixed film aerobic treatment).

Table 2.3 summarises units operations used in physico-chemical treatments. Some more information on this issue can be found in the Common waste water and waste gas treatment BREF (CWW).

Unit operation	Purpose	Principle of operation
<i>Separation operations</i>		
Acid break-up of emulsions	The term 'acid break-up' is understood to be the treatment of emulsions. The aim of the treatment is the separation of the emulsion into waste water, oil/grease and undissolved metals as hydroxide sludge	
Centrifugation	Dewatering metal salt sludges from precipitation techniques	Separates solids and liquids by rapidly rotating the mixture in a vessel. Solids either settle at the bottom (sedimentation - type) or adhere to the inside wall of the vessel (filtration - type) through which the liquid passes
Evaporation and distillation	Evaporation and distillation are similar processes with different objectives. During evaporation the useful material in a mixture is evaporated through thermal effects and captured as vapour and generally condensed. Distillation is a separation process, which is used for the separation of mixtures, which obtains better separation ratios than evaporation	The aim of evaporation/distillation is to separate the oil into a good usable form. In the Ph-c plants, evaporation is used as a partition stage in order to separate vaporisable materials from the waste water. Depending on the ingredients of the waste water, evaporation can also be used as conditioning for a further preparation stage, such as membrane filtration. Evaporator technology is of great importance whenever organic solvents are to be separated from the waste to be treated
Extraction		Extraction is used for the specific separation of components from a mixture of substances. The mixture of substances is thoroughly mixed with a selective solvent. During mixing, the component from the mixture of substances migrate into the extracting agent. With the subsequent separation of the extracting agent from the substance mixture, finally the components of the mixture are also separated
Filtration/dewatering	This is the most common operation applied, e.g. in drinking water treatment, industrial waste water treatment	Involves passing a mixture of liquid and solids (or gas and solids) through a filter medium to trap the solids. Different kinds of filters exist, such as gravel filters, sand filters and mechanical filters (e.g. waste water screen presses, chamber filter presses, membrane filter presses)
Filtration/sieving	The sieving of the waste to be treated is essential for the protection and safety of functional units, such as pumps, sluice gates, valves	Sieving is a classifying/separating procedure with which the filtered material – liquid/solid mixture (slurry) – is separated into two mixtures, one with an average particle size smaller than the input, and another larger than the input

Unit operation	Purpose	Principle of operation
Filtration (by membranes)	Separation of substances/solids from liquid mixtures. Ultrafiltration can be used for break-up of emulsions	In membrane procedures the liquids to be treated are fed under controlled pressure and current conditions past a semi-permeable membrane. The separative power of the membrane is essentially based on the filtering effect and thus outputs are neither altered biologically nor chemically.
Flotation	Used by refining, meat packing, paint, paper milling and baking industries	Introduction of tiny air bubbles into a solution containing suspended particles. Particles attach to air bubbles and float
Ion exchange processes	Ion exchange is a process for the cleaning of liquid waste of dissolved electrically charged particles (ions) by means of ion exchanger materials. Can also be used in water-softening, as Ca and Mg ions are removed from the liquid stream. Some of substances suitable for ion exchangers are liquid waste from the electroplating industry, chromium electrolytes/chromating baths, phosphoric acid pickling, hydrochloric acid pickling and sulphuric acid anodising baths. Groups of material unsuitable for ion exchangers are: organic compounds as these can irreversibly block the resins in the exchanger or whose removal may be incomplete; strong oxidising agents, as these may damage the anion exchanger resins; metal cyanide complexes, as strong base anion exchangers damage the resins; aromatic and halogenised hydrocarbons, as they cause the exchanger resins to swell at times and thus can lead to interruptions in the exchanger availability.	Ion exchange resins have the ability to exchange their settled groups of ions (cations or anion) with ions contained in the water
Oil separation processes	Gravity settlement without heat to produce an oil rich layer, that is skimmed off and sent to oil recyclers for further processing, and an aqueous phase plus sludge that is processed through the main plant. At some plants, this is a major part of the day-to-day activities. At others it is an occasional batch process and only operated when needed to provide a full service to major customers but where the company does not actively seek oil/water streams for treatment. Some sites add acid to the oil to assist in the separation process (emulsion breaking)	Gravity separation of soluble oils and oil/water mixtures

Unit operation	Purpose	Principle of operation
Organic splitting of emulsions		For the destabilisation of the emulsifying agent, polyelectrolytes and/or similar products are used. These allow good splitting of the emulsion comparable to acid splitting
Reverse osmosis	Used to produce drinking water from brackish groundwater and seawater. Also for recovery of electroplating chemicals from plating rinse-water and sulphate from paper industry waste water. Used in leachate treatment	Uses a mechanical force, e.g. high pressure (17 – 100 atm) to drive solvent (usually water) through a membrane. This generate two fractions one that concentrate the dissolved components and another where the solvent is purified
Screening	Waste water containing solids, etc.	Removes large particles from waste water. There are three types of screens, rotating drums, vibrating and stationary
Sedimentation	Sedimentation is used in Ph-c plants specifically for the thickening of sludges, and the separation of heavy particles and suspended matter from the waste water and concentrate sludge	The forces of gravity cause the thicker phase of a suspension to separate. To this extent, the nature of the force determines the type of sedimentation: gravity sedimentation or centrifugal sedimentation
Sorption (absorption and adsorption)	If the waste water shows increased and/or inadmissibly high values of TOC, AOX or PCB, the organic materials generally separated using adsorption	Sorption is the uptake of a substance (gas, vapour, liquid) by another material, as a result of the contact of both materials. Absorption is designated as the penetration of a gas into a solid or liquid phase (absorbents) by diffusion. Adsorption is described as the accumulation of gases or solute materials at the surface of a solid or liquid material (adsorbents) by molecular forces. Adsorption is a physical process, and to this extent the chemical characteristics of the adsorbed material are unaltered
Stripping (by air or steam)	Stripping is used in order to be able to use the following procedures better and more effectively; or as a final stage to reduce the concentration of certain hydrocarbons (AOX). By stripping, volatile materials, for example hydrogen sulphide (H <sub>2</sub> S), ammonia (NH <sub>3</sub> ), low boiling hydrocarbons and chlorine hydrocarbons (AOX) can be separated from aqueous solutions	Stripping is the driving out of easily vaporisable materials from liquid mixtures. Air or water vapour is used for stripping, with a simultaneous increase of the phase-boundary surfaces. Stripping is thus a separation process in which the separated material is in the exhaust air (stripping with air) or in the distillate (stripping with water vapour)
<b>Chemical processes *</b>		
Electrolysis	The recovery of metals from solutions (e.g. silver from photographic waste)	Use of electrical power to reduce metals from solution

Unit operation	Purpose	Principle of operation
Neutralisation	To neutralise the waste water or to recuperate some components from it by precipitation at a specific pH(s). Depending on equipment configuration, neutralisation and sedimentation can be carried out in the same container	Neutralisation is the adjustment of the pH values to a neutral level, for instance, pH ~ 7. Neutralisation is achieved by adding acids or alkalis to the material to be neutralised and/or by the mixing of acids and alkalis
Oxidation/reduction	Redox reactions in connection with the Ph-c treatment of waste activity involve the detoxicating of nitrite and cyanide (oxidation) and chromium (VI) compounds (reduction). Other possible treatments are the destruction of sulphides or peroxides. Wastes are made less toxic, simpler and less volatile by subtracting or adding electrons between reactants	Oxidation and reduction are processes which are generally coupled. Oxidation is the release of electrons, and reduction is the uptake of electrons.
Precipitation/flocculation	The separation of dissolved or suspended materials (e.g. metals) by the addition of chemicals	Precipitation is the conversion of a solute substance to an undissolved substance, in general by the addition of chemicals. Flocculation is the agglomeration of more or less fine particles (as well as solute substances) into larger flocs; these are separated by sedimentation or filtration
Wet air oxidation	Sewage sludge	Solids solubilised and oxidised under high pressure
* Some of these treatments induce separations (e.g precipitation)		

**Table 2.3: Unit operations used in physico-chemical treatments**  
[80, Petts and Eduljee, 1994], [121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004]

## 2.3. Physico-chemical treatments of waste solids and waste sludges

The main goal in the physico-chemical treatments of waste solids and waste sludges is to minimise the long-term release by leaching out the primarily heavy metals and low biodegradable compounds. The available treatment options act to prolong the leaching time period by releasing, for example, heavy metals at lower and more environmentally acceptable concentrations for an extended period of time.

In principle, all treatment options can be applied to waste solids and waste sludges. However, the characteristics of the treated material and the effectiveness of a treatment technology can vary greatly depending on the specific properties of the original waste IN and on the type of cleaning system applied. The treatment options has been sub-grouped according to the following types:

- extraction and separation
- thermal treatment
- mechanical separation
- conditioning
- immobilisation (this treatment covers solidification and stabilisation)
- dewatering
- drying
- thermal desorption
- vapour extraction from excavated soil
- solvent extraction from solid waste (e.g. excavated soil)

- 
- excavation and removal of excavated soil
  - soil washing.

### **2.3.1. Extraction and separation**

#### **Purpose**

To extract heavy metals and salts from solid wastes, using acid.

#### **Principle of operation**

Solubilises compounds and removes them with water.

#### **Feed and output streams**

Treatment options using extraction and separation processes can, in principle, cover all types of processes extracting specific components from the wastes.

#### **Users**

Several techniques have been proposed both in Europe and in Japan for air pollution control residues.

### **2.3.2. Thermal treatments**

#### **Purpose**

Thermal treatment of FGT waste from combustion processes is used extensively in a few countries, mainly to reduce the volume and to improve their leaching properties.

#### **Principle of operation**

High temperature treatments use heat in order to melt waste and initiate vitrification and ceramisation processes. Thermal treatments can be grouped into three categories: vitrification, smelting and sintering. The differences between these processes chiefly relate to the characteristics and properties of the final material:

- vitrification is a process where wastes are mixed with glass precursor materials and then combined at high temperatures into a single-phase amorphous, glassy output. Typical vitrification temperatures are 1300 to 1500 °C. The retention mechanisms are chemical bonding of inorganic species in the waste with glass-forming materials, such as silica, and encapsulation of the constituents by a layer of glassy material
- melting is similar to vitrifying, but this process does not include the addition of glass materials and results in a multiple-phased product. Often several molten metal phases are generated. It is possible to separate specific metal phases from the melted output and recycle these metals, possibly after refinement. Temperatures are similar to those used in vitrifying
- sintering involves heating the waste to a level where a bonding of the particles occurs and chemical phases in the wastes reconfigure. This leads to a denser output with less porosity and a higher strength than the original waste. Typical temperatures are around 900 °C. Temperatures for sintering bottom ash from MSW incinerators can be up to 1200 °C.

#### **Feed and output streams**

Most commonly, FGT wastes are treated thermally in combination with bottom ashes.

#### **Process description**

Regardless of the process, the thermal treatment of FGT waste in most cases results in a more homogeneous, denser product with improved leaching properties. Vitrifying also adds the benefits of the physical encapsulation of contaminants in the glass matrix.

The thermal treatment of FGT waste requires substantial off gas treatment, thus creating a new solid residue to be treated. Also the high salts concentrations in FGT waste can cause corrosion problems in off-gas treatment systems.

### Users

Sintering is not used as a dedicated treatment option for FGT waste, however some combined treatment methods may involve sintering.

## 2.3.3. Mechanical separation

### Purpose

The aim of the treatment is to generate a material which is inert, does not negatively affect water bodies, and has the potential for safe recovery, e.g. as a soil substitute or in road construction. Such treatment reduces the mass of waste for disposal. Furthermore, the clean separated and collected ferrous and non-ferrous metal fractions can be re-used. In addition, the reduction in the amount of heavy metals, e.g. arsenic (salt) being emitted in the environment, is also a major benefit.

### Principle of operation

In the case of bottom ash treatment, the bottom ash is separated into at least three fractions: mineral compounds, unburned material and scrap metal. A reduction of heavy metals and soluble compounds is required and is important for re-use of the material after treatment. The water soluble components are the most water-relevant ingredients of bottom ash.

### Feed and output streams

One of the main products of waste incineration is the bottom ash generated through the burning process. An input of one tonne of household waste generates approximately 250 - 350 kg of bottom ash. The bottom ash is generally composed of components such as chloride, arsenic, lead, cadmium, copper, mineral materials and scrap metals.

### Process description

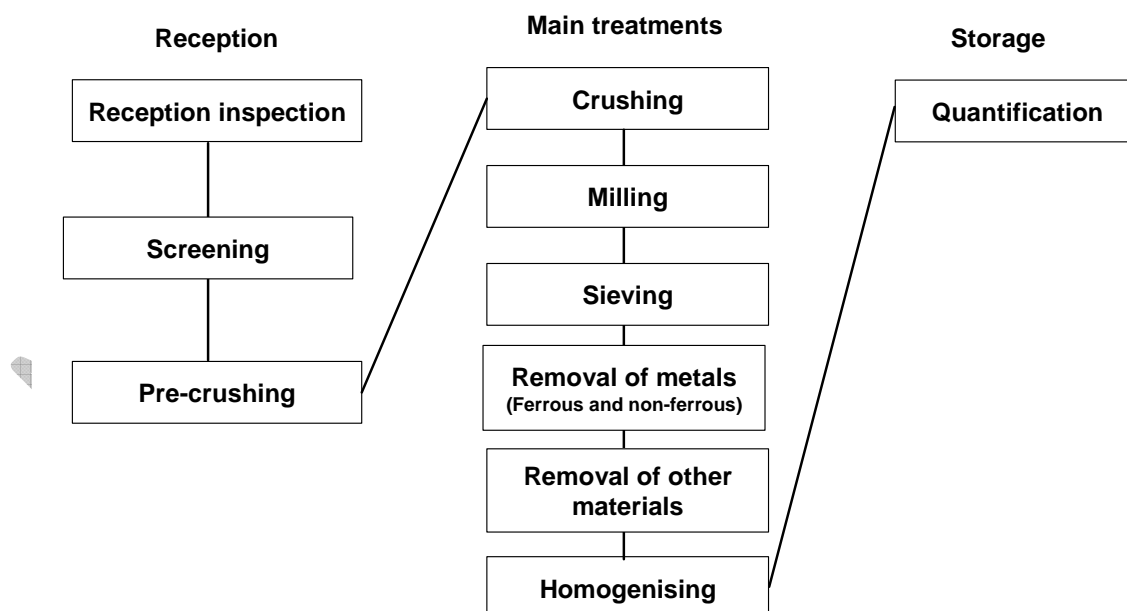


Figure 2.2: Example of some mechanical separations used for the treatment of bottom ashes [89, Germany, 2003], [150, TWG, 2004]

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**Users**

Bottom ash and FGT waste.

### **2.3.4. Conditioning**

**Purpose**

The aim is the treatment of the solid and paste like wastes for recovery/disposal in incineration plants or for landfilling.

**Principle of operation**

The substances that can only be incinerated or landfilled are conditioned by means of aggregates. Depending on the final disposal plant (e.g. incineration or landfill); diatomite, sawdust or other appropriate aggregates are added to the waste.

**Process description**

Wastes with certain resource contents may be passed on to the downstream plant for the recovery of recyclable substances. If necessary, the wastes may be run over a one step crushing, e.g. in order to crush the metal packaging such as paint cans, and transfer them via a conveyor system to the facility for recovery of recyclable material.

Wastes that are delivered in large capacity containers are pretreated in a second crushing facility. For dusty wastes, a third fully encapsulated two-shaft shredder is available. In the free-falling mixer, the pretreated wastes may be mixed with aggregates to produce a batch of maximum  $10 \text{ m}^3$ . The free-falling mixer consists mainly of an open cylindrical-conical container with a volume of  $20 \text{ m}^3$ . This container is filled via the last conveyor of the charging system. Rotation of the container produces a homogeneous mixture and the abrasive forces in the mixing drum cause a quasi-dry cleaning of metal and plastic components in the waste. The free-falling mixer is emptied into the loading facility which conveys the conditioned waste either to truck loading or to further treatment towards the facility for the recovery of recyclable substances.

**Users**

Preparation of waste to be used as fuel.

### **2.3.5. Immobilisation**

**Purpose**

The aim of immobilisation is to minimise the rate of contaminant migration to the environment and/or to reduce the level of toxicity of contaminants, in order to alter or improve the characteristics of the waste so that it can be disposed of. The objective encompasses both a reduction in the waste toxicity and mobility as well as an improvement in the engineering properties of the stabilised material.

**Principle of operation**

Immobilisation relies on the properties of the reagent to produce an immobilised waste product, even where the waste product does not have a solid form. These processes retain substance(s) adsorbed to, or trapped within, a solid matrix. Some of these processes are reversible (i.e. the immobilised substances can be released), due to both poor process control and to subsequent mixing with other waste types. Two types of processes have been developed. These are commonly referred to as: stabilisation and solidification.



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### Stabilisation

This is a process by which contaminants (e.g. heavy metals) are fully or partially bound by the addition of supporting media, binders, or other modifiers. Stabilisation is accomplished by mixing the waste with a reagent (depending on the type of waste and reaction planned, this can be, for example, clay particles; humic organic substances, such as peat; activated carbon; oxidisers; reductors; precipitating reagents) to minimise the rate of contamination migration from the waste, thereby reducing the toxicity of the waste and improving the handling properties of the waste at the landfill. To achieve this, a process should include a physico-chemical interaction between the reagent and waste, rather than just a dilution.

These stabilisation methods make use of both the precipitation of metals in new minerals as well as the binding of metals to minerals by sorption. The process includes some sort of solubilisation of the heavy metals in the material and a subsequent precipitation in or sorption to new minerals.

The physical mechanisms used in stabilisation are: macro-encapsulation, micro-encapsulation, absorption, adsorption, precipitation and detoxification. There is an extensive range of sorbents and binders available for such purposes. Some of the most commonly used are: cement, pozzolans (alumino-silicious material that reacts with lime and water), lime, soluble silicates, organically modified clays or lime, thermosetting organic polymers, thermoplastic materials and vitrification (in-situ or in-plant).

In many cases, both types of reagents (chemical reagents as mentioned three paragraphs above) and sorbents and binders (as mentioned in the above paragraph) are used simultaneously.

### Solidification

Uses additives to change the physical properties of the waste (as measured by its engineering properties such as strength, compressibility, and/or permeability). The term 'solidification' (and encapsulation or fixation) relate to the mixing of wastes with a reagent (pulverised fuel ash; cement, lime; blast furnace slag; cement kiln dust; organic binders such as bitumen/asphalt or paraffin; and polyethylene) to produce a solid waste form (with low porosity and low permeability matrix) for landfill disposal. Substances are either adsorbed to the reagent or trapped within the waste form. The output should possess a high resistance to chemical and biological degradation processes that could lead to the release of contaminants.

The addition of cement, for example, generally decreases the hydraulic conductivity and porosity of the material, and in addition increases tortuosity, durability, strength and volume. However, it usually increases the pH and alkaline capacity of the mixture, therefore improving the leaching behaviour of the product (e.g amphoteric metals, some organic compounds). In some cases, depending on the binder, solidification may result in chemical changes of the material matrix.

In summary, the fixation and insolubilisation of the pollutants is realised by means of four mechanisms: precipitation, complexation, encapsulation and adsorption.

### Feed and output streams

This technology is applied for many inorganic wastes (typically hazardous waste) present in industry such as:

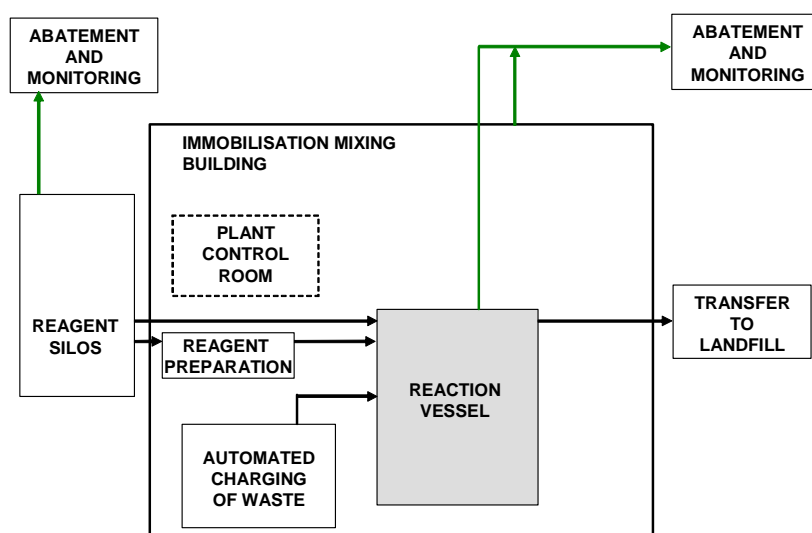
- pasty waste and slurries containing inorganic components (heavy metals, etc.) and small amounts of non-soluble organics (polycyclic aromatics, fuel waste, etc.) For example, complex liquid and solid waste contaminated with heavy metals (Cu, Pb, Cd, Hg, Cr, etc.)
- solid and dry waste with inorganic components (in this case hydration water must be added). For example, contaminated soil and filter cakes; refuse with very few non-soluble hydrocarbons; bottom ashes and slag; FGT waste
- solidification is sometimes used for mixing various viscous liquids, such as glues and pastes, with sawdust to produce a solid crumb suitable for landfill. Such practice is not allowed, on landfill sites, in some countries, such as France, Germany and the Benelux Union. In some cases, such components are mixed with cement and lime or other suitable binder material.

Wastes that are legally not accepted by the Landfill Directive to be treated by immobilisation on installations located on landfill sites, are liquid wastes, waste containing toxic components, volatile compounds, foul smelling components or explosives. Key issues for immobilisation include: the suitability of the waste, the process control, the emissions generated and the output specification. Under the Landfill Directive (EC/33/2003) and its annexes, the output specification needs to be aligned with the acceptance criteria for the receiving landfill, which are developed by the European Technical Adaptation Committee and which will cover leachability, physical stability and reaction with other wastes. Their transcription into national legislation is due by the end of 2005.

The resulting output of solidification can either be landfilled or allowed to solidify in a holding area prior to landfill. The final stabilised/solidified waste is usually landfilled directly or sometimes cast into blocks (e.g. at a size of 1 m<sup>3</sup>) before landfilling.

### Process description

The process typically comprises storage of the reagents, a reaction vessel and in some cases the addition of water. Figure 2.3 shows a representation of a typical immobilisation process.



**Figure 2.3: Representation of an immobilisation process**  
[55, UK EA, 2001]

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Several of the stabilisation methods have an initial washing step, where a major part of soluble salts and to some extent metals are extracted before chemical binding of the remaining metals. These methods are finalised by dewatering the stabilised product, which will then be ready for landfilling.

Two solidification processes are widely used: a) cement solidification (the most prevalent solidification technique), based on mixing waste with cement, and b) special hydraulic binder processes, which are chemical processes, aimed at developing bonds between the binder and the waste. Another technique, also in large-scale use, includes, e.g. the curing of fly ash waste with aqueous neutral or acidic liquors to give a granular output prior to landfill.

#### **Users**

Immobilisation treatments (both stabilisation and solidification) are applied to:

- remediation of hazardous waste sites
- treatments of waste from other treatment processes (e.g. ash from thermal treatments, residues from end-of-pipe techniques)
- treatment of contaminated land where large quantities of soil containing contaminants are encountered.

In several EU countries stabilisation/solidification is not an issue at all due to their national legislation. In these cases, a lot of wastes do not need any such treatments to respect the parameters of the annexes of the EU Landfill Directive or national legislation.

Radioactive wastes have been encapsulated using cement/pulverised fuel ash and bottom ash (slag) for more than 30 years. However, radioactive materials are explicitly excluded from the IPPC Directive.

### **2.3.6. Dewatering**

#### **Purpose**

Sludge dewatering increases the dry solids content of sludge producing a 'solid' waste. It is a grey area as to when a liquid sludge becomes a solid waste; however, any sludge typically over 10 % dry solids becomes difficult and expensive to pump.

#### **Principle of operation**

Dewatering at ratios typically higher than 10 % will first require some form of chemical conditioning to assist in the separation of the bound and entrained water from within the sludge. There is a wide range of high molecular weight polymeric flocculants that are particularly effective at improving dewatering performance.

#### **Feed and output streams**

Dewatering produces a sludge 'cake', which may be between 20 – 50 % dry solids, and an aqueous waste stream. Overall disposal costs would be expected to be reduced in cases where the aqueous waste stream requires no, or minimal, additional processing to remove contaminants.

#### **Process description**

A number of sludge dewatering processes exist and selection depends upon the nature and frequency of the solids produced, and the sludge cake required, e.g.

- filter (or plate) presses, which are batch processes and can be manually intensive. A filter press can produce up to 40 % dry solids cake

- the belt press, which is a continuous process with the filter cloth continually running through rollers that forcefully dewater the sludge. A belt press can produce up to 35 % dry solids cake
- centrifuges, also continuous processes that can produce a cake of up to 40 % dry solids for certain sludges. Because of the shear forces, it can break up the solid particulates
- filter drums.

#### **Users**

The majority of sites use filter presses on the sludge from the treatment plant and then send the aqueous fraction through clarification or DAF units prior to sewer discharge. Excess solids are returned to the treatment tanks.

### **2.3.7. High temperature drying**

#### **Purpose**

The aims of the process are the following:

- removal of the water content from the wastes; making recycling economically viable
- concentration of the waste components (e.g. metal compounds); the heating value is considerably raised
- elimination of the problems with handling paste-like substances, as drying the waste transforms it into granulate material
- use of the waste heat in other processes, e.g. distillation
- the dissipated plume gives the necessary moisture to the biofilter.

#### **Principle of operation**

The input substances that are to be dried are provided by the gathering chain conveyor and put into the revolving tube drum in single portions. The residence time of the input substances in the drier and thus the dryness of the granulated product can be regulated by hydraulic adjustment of the tube angle. The energy required for the drying process is drawn from the waste heat of the incinerator. The air needed for cooling the flue-gases is cooled down to 150 °C in air-air heat exchangers.

Up to 30000 m<sup>3</sup>/h drying air (maximum 100 °C) flow through the revolving tube countercurrently to the moist input. The heat is used for the evaporation of the water. The plume is extracted by suction via a dust filter and directly transferred to the biofilter. Hereby, a slight negative pressure is created in the dryer who prevents effectively the leakage of dust into the environment. The granulated dry product is discharged automatically by the rotation of the drum and filled into big bags or other containers.

#### **Feed and output streams**

Sludges are dried and transformed into granulated material.

#### **Process description**

Drying consists of the following processes:

- warm air supply controlled by temperature and differential pressure
- hydraulically adjustable revolving tube drum
- gathering chain conveyor for charging
- dust filter with 300 m<sup>2</sup> filter area
- plume dissipation towards biofilter by means of induced draft fan
- measurement technique (e.g. dust, temperature, pressure, volume flow and moisture)
- process control system.

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### 2.3.8. Thermal distillative drying plants

#### Purpose

To process materials which cannot be accepted by hazardous waste incineration plants or hazardous waste landfill sites without complex prior conditioning.

#### Principle of operation

The input material is first crushed in the plant under inert conditions and bunkered. The released propellants are transferred to the high temperature incineration plant or to the biofilter. Afterwards, treatment is carried out in order to distillate the fluids from the input material.

#### Feed and output streams

Solid/paste like hazardous wastes which contain considerable amounts of free or bound fluids are treated. Both the solid and the fluid products that leave this facility may be recycled, thermally used, incinerated or landfilled.

#### Process description

The process consists of two parts: materials handling and crushing; and thermal distillation.

- Material handling and crushing:
  - lift-tilt installation for containers
  - inerteable crusher
  - gathering conveyor
  - CO<sub>2</sub> fire extinguisher and inerting facility
  - discharge of solids with load container and carrying chain conveyor.
- Thermal distillation:
  - reactor and vacuum slider
  - plume filter and circulation fan
  - plume superheater
  - condensers, product coolers, product containers and phase separation
  - vacuum pump station
  - vapour, inert gas and cooling water distribution
  - exhaustive security measures
  - control system with two work places and one computer for data collection.

The containers are transported from the high rack storage area to the facility and individually emptied into the feeding hopper of the crusher. After crushing, the input material is stored under a CO<sub>2</sub> atmosphere on an inerted gathering conveyor. This is carried out until the quantity necessary for processing is reached in the mixing reactor (maximum 3 m<sup>3</sup>) and the reactor is prepared for take-up of the next load. The waste solvent vapours released at the crusher are specifically drawn off in order to prevent the production of explosive mixtures in the hall. The drawn off air is fed to the biofilter as well as the exhaust air from the vacuum pumps.

If the mixing reactor has been re-inerted after emptying of the previous load, it can be charged by the gathering conveyor. After charging, the mixing reactor and the pipe system are pressurised by the vacuum pumps to 400 mbar. Then, the circulation fan is powered up. The nitrogen from inerting and the created plumes can then be run over the superheater where they are heated up to 450 °C. Afterwards, they flow into the reactor where they heat up and dry the input material. The heating period may, if necessary, be supported by fresh vapour from a boiler. Vacuum control keeps the maximum pressure in the facility approximately at 100 mbar, below that of the ambient air.

At the end of the drying process; i.e. when the maximum temperature of 180 to 200 °C is reached in the reactor, in the plume filter or in the circulation fan; the facility is evacuated to a pressure of <100 mbar. This is carried out in order to evaporate the remaining solvent residues and to cool the dried material. To keep the emissions of the dried material low at discharge, cooling water is added directly to the dried material. Here, it immediately evaporates under vacuum and thus cools the dry product down to the discharge temperature of 50 to 60 °C. The condensate is recovered by the in-house distillation facility directly after phase separation or after treatment. Solvent fractions that cannot be recycled may be thermally utilised or incinerated in the in-house high temperature incineration facility.

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### 2.3.9. Thermal desorption

#### **Purpose**

To separate relatively volatile compounds from solid waste.

#### **Principle of operation**

In the thermal desorption process, volatile and semi-volatile contaminants are removed from soils, sediments, slurries, and filter cakes. Typical operating temperatures are between 175 - 370 °C, but temperatures from 90 to 650 °C may be employed. Thermal desorption promotes physical separation of the components rather than combustion.

#### **Feed and output streams**

Soils contaminated with non-biodegradable organic compounds, soil contaminated with petroleum fuels, soil contaminated with hazardous wastes and tar containing asphalt or similar waste are the types of waste processed by this treatment. The contamination is transferred to a further treatment.

Thermal desorbers effectively treat soils, sludges, and filter cakes and remove volatile and semi-volatile organic compounds. Some higher boiling point substances such as PCBs and dioxins may also be removed (if present). Inorganic compounds are not easily removed with this type of process, although some relatively volatile metals such as mercury may be volatilised. The temperatures reached in thermal desorbers generally do not oxidise metals.

#### **Process description**

After contaminated soil is excavated, the waste material is screened to remove objects greater than 4 to 8 cm in diameter. Direct or indirect heat exchange vaporises the organic compounds, producing an off-gas that is typically treated before being vented to the air. In general, any one of four desorber designs are used: rotary dryer, asphalt plant aggregate dryer, thermal screw, and the conveyor furnace. The treatment systems include both mobile and stationary process units designed specifically for treating soil, and asphalt aggregate dryers that can be adapted to treat soils. Mobile systems are most often used, due to reduced soil transportation costs and to allow for backfilling of the treated soil. However, stationary systems are also available and it may be feasible to provide regional services. The desorbed gases may be incinerated.

#### **Users**

Treatment of contaminated soils and tar containing asphalt and similar waste.

### 2.3.10. Vapour extraction

#### **Purpose**

Vapour extraction can be used as a method for treating solid waste, e.g. excavated contaminated soil, with volatile hydrocarbons.

#### **Principle of operation**

In general terms, vapour extraction removes volatile organic constituents from contaminated waste by creating a sufficient subsurface airflow to strip contaminants from the vadose (unsaturated) zone by volatilisation. As the contaminant vapours are removed, they may be vented directly to the air or controlled in a number of ways.

#### **Feed and output streams**

Vapour extraction has been widely used to treat excavated soil contaminated with gasoline or chlorinated solvents (e.g. TCE). It is also sometimes used to minimise the migration of vapours into structures or residential areas during some other in-situ remediation not covered in this document.

Spills or leaks of fuels typically involve liquids containing dozens of different constituents. For removal by this treatment to be effective, the contaminants must generally have vapour pressures greater than 1.0 mm Hg at - 7 °C. Complete removal of contaminants may not be possible with this technique alone.

#### **Process description**

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The success of the treatment for a given application depends on numerous factors with the two key criteria being: the nature of the contamination and the nature of the waste (e.g. soil). The tendency of the organic contaminants to partition into water or to be adsorbed onto soil particles also affects its effectiveness, and hence the compound's water solubility, Henry's Law constant, and the sorption coefficient to the solid waste are of interest. The temperature affects each of these variables and hence, the rate of vapour diffusion and transport. Increasing the temperature is one option commonly considered for enhancing the treatment performance. Solid waste can be heated in one of three ways: 1) introduction of heated air or steam, 2) input of electromagnetic energy through the waste, or 3) heat release through a chemical reaction. The use of heated air or steam appears to be the most widely used approach.

Typical systems include extraction, monitoring, air inlet, vacuum pumps, vapour treatment devices, vapour/liquid separators, and liquid-phase treatment devices.

#### **Users**

Vapour extraction has been used successfully for several years as a combined two-phase treatment of both groundwater and contaminated soil, and is increasingly being employed. Although this treatment may be used for a variety of soil types, its effectiveness depends on the ability of air to flow through the soil.

### **2.3.11. Solvent extraction**

#### **Purpose**

'Solvent extraction' is much more effective for treating organic compounds than inorganic compounds and metals. It can be used in conjunction with other processes to reduce remediation costs.

#### **Principle of operation**

Solvent extraction differs from soil washing in that it employs organic solvents (e.g. propane, butane, carbon dioxide, aliphatic amines (e.g. triethylamine)) rather than aqueous solutions to extract contaminants from the soil. Like soil washing, it is a separation process that does not destroy the contaminants. It works as the contaminants will have a greater solubility in the solvent than in the soil.

#### **Feed and output streams**

Sediments, sludge, and soils contaminated with volatile organic compounds (VOCs), petroleum wastes, PCBs, and halogenated solvents can be effectively treated with solvent extraction. The removal of inorganic compounds such as acids, bases, salts, and heavy metals is limited, but these types of compounds usually do not hinder the remediation process. Metals may undergo a chemical change to a less toxic or leachable form, however their presence in the waste streams may still restrict disposal and recycle options.

Whilst these separation processes may be more effective in treating soils contaminated with petroleum fuels, they are generally employed to treat soils containing metals or heavy organic compounds.

The concentrated contaminants can be analysed and subsequently designated for further treatment, recycling, or re-use before disposal. While solvent extraction may improve the condition of the solids, often they may still need dewatering, treatment for residual organic compounds, additional separation, stabilisation, or some other treatment. The water from the dewatering process, the solids, and the water from the extractor will need to be analysed to aid in the choice of the most appropriate treatment and disposal.

#### **Process description**

The remediation process begins with excavating the contaminated soil and feeding it through a screen to remove large objects. In some cases, solvent or water is added to the waste in order to aid pumping it to the extraction unit. In the extractor, solvent is added and mixed with the waste to promote the dissolving of the contaminants into the solvent. Laboratory testing can determine which solvent adequately separates the contaminants from the soil. Generally, the solvent will have a higher vapour pressure than the contaminants (i.e. a lower boiling point) so that with an appropriate pressure or temperature change, the solvent may be separated from the contaminants, compressed, and recycled to the extractor.

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**Users**

Treatment of contaminated soil.

### **2.3.12. Excavation and removal of contaminated soil**

**Purpose**

Excavation activities may be carried out in isolation but are also typically carried out as part are of the on-site treatment processes such as incineration, thermal desorption, ex-situ biotreatment, and certain physico-chemical treatments.

**Principle of operation**

If removal of the contaminated soil is the selected remedy, the excavated soil is typically transported off site for subsequent disposal in a landfill.

**Feed and output streams**

Contaminated soils and decontaminated soil.

**Process description**

Typical civil engineering machinery is used.

**Users**

The excavation and removal of soils contaminated with fuels is a common practice.

### **2.3.13. Soil washing**

**Purpose**

Soil washing is carried out to separate the decontaminated fractions and pollutants.

**Principle of operation**

Soil washing is an ex-situ process in which contaminated soil is excavated and fed through a water-based washing process. It operates on the principle that contaminants are associated with certain size fractions of soil particles and that these contaminants can be dissolved or suspended in an aqueous solution or removed by separating out clay and silt particles from the bulk soil. Additives such as surfactants or chelating agents are sometimes used to improve the separation efficiency (the treatment using additives may be referred to as chemical extraction). The aqueous solution containing the contaminants is treated by conventional waste water treatment methods.

The process is a water-based process and removes contaminants from soils in one of two ways:

- a. by dissolving or suspending them in the wash solution (which is treated later by conventional waste water treatment methods)
- b. by concentrating them into a smaller volume of soil through particle size separation, gravity separation, and attrition-scrubbing (similar to the techniques used in the mineral processing industry).

The concept of reducing soil contamination through the use of particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically, to clay, silt, and organic soil particles. The silt and clay are attached to sand and gravel particles by physical processes, primarily compaction and adhesion. Washing processes that separate the fine (i.e. clay and silt) particles from the coarser (i.e. sand and gravel) soil particles effectively separate and concentrate the contaminants into a smaller volume of soil that can be easier further treated or disposed of.

**Feed and output streams**

Soil washing is effective for a wide range of organic and inorganic contaminants, including petroleum and fuel residues. Removal efficiencies range from 90 – 99 % for volatile organic compounds (VOCs) and from 40 – 90 % for semi-volatile compounds. Compounds with low water solubilities such as metals, pesticides or PCBs sometimes require acids or chelating agents to assist in the removal. Some pilot scale projects on radionuclides pollution



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treatment have been reported. The washing process is also applicable for contaminated sand and gravel from construction and demolition waste.

While these separation processes may be more effective in treating soils contaminated with petroleum fuels, generally they are employed to treat soils containing metals or heavy organic compounds.

Soil washing may can be effective for the remediation of soils with a small amount of clay and silt particles, but large amounts of clay and silt particles mitigate the effectiveness of soil washing.

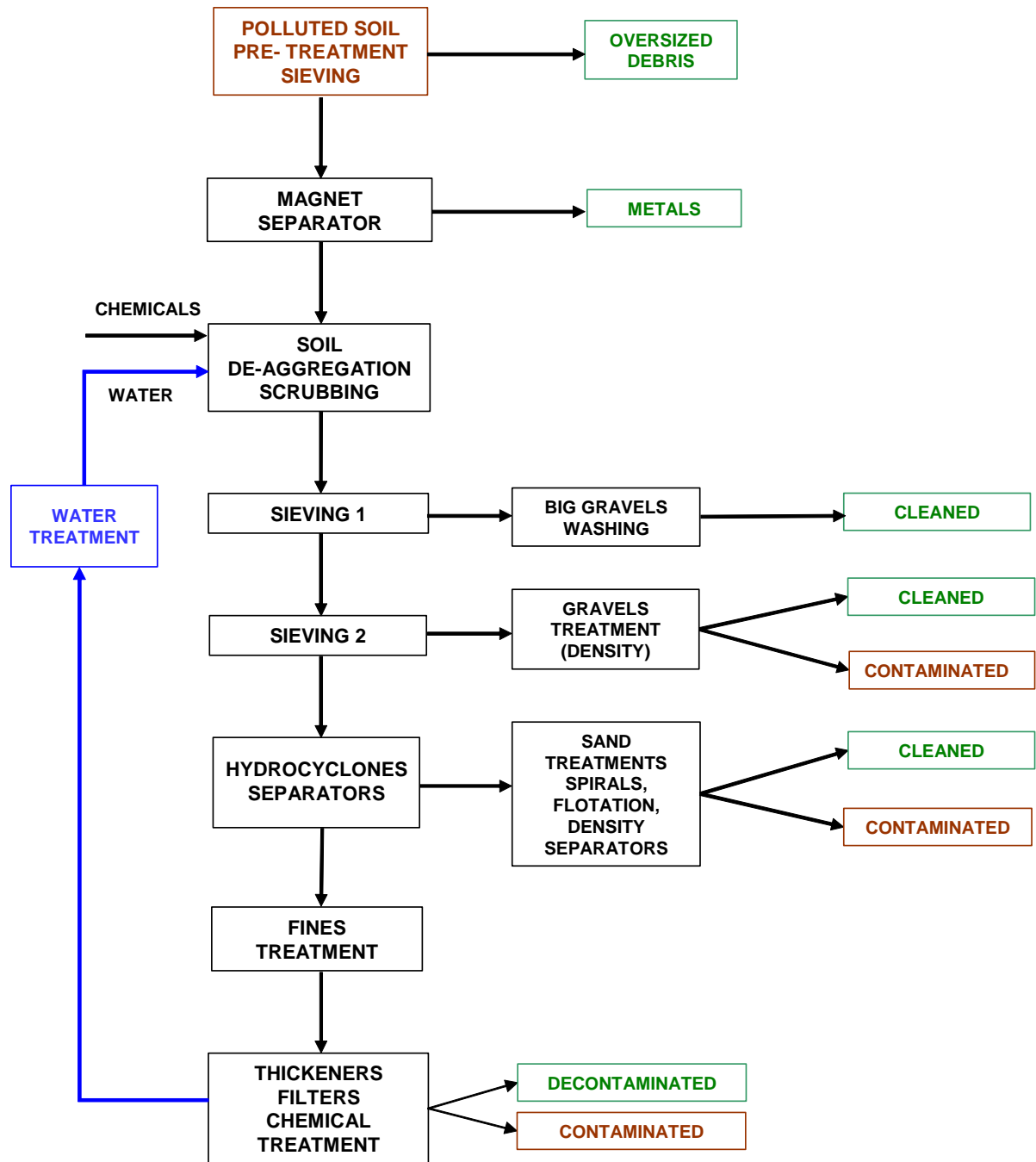
**Process description**

The excavation and removal of debris and large objects precedes the soil washing process. Sometimes water is added to the soil to form a slurry that can be pumped. After the soil is prepared for soil washing, it is mixed with wash-water, and extraction agents are sometimes added.

After separation from the wash-water, the soil is rinsed with clean water and may be returned to the site. The suspended soil particles are removed by gravity from the wash-water as sludge. Sometimes flocculation is used to aid in sludge removal. This sludge is more highly contaminated than the original soil and undergoes further treatment or secure disposal. The spent wash-water from which the sludge is removed is treated and recycled. Residual solids from the recycling process may require further treatment.

Figure 2.4 presents a general flow scheme of a soil washing plant.

NON OFFICIAL FEAD VERSION



**Figure 2.4: General flow scheme of a soil washing plant**  
[123, Perseo, 2003]

Typically, soil washing segregates a soil into a small volume of highly contaminated silt and clay and a larger volume of cleaned coarser soil.

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Physical separation methods are mechanical methods for separating mixtures of solids to obtain a concentrated form of some constituents. Physical separations include screening, attrition scrubbing, or using hydrogravimetric separators as such hydrocyclones, jigs, spiral classifiers. In addition, in the majority of cases, the processes use water based chemical agents, which provide both dispersion and extraction. Chemicals (dispersants, collectors, frothers, etc.) may be added in some cases to enhance the quality of the separation.

#### **Users**

The soil washing technique is very well established in the Netherlands, Germany and Belgium, due to the sandy structure of the local soils. In 2003, eight plants in the Netherlands, six in Germany and six in Belgium were in operation. The technology is starting to become more developed in Switzerland and in northern Italy. Most plants have a capacity of 30 - 60 tonnes an hour. Furthermore, numerous on-site remediation projects have been performed with mobile plants, presenting usually smaller capacities (from 10 to 30 tonnes per hour).

### **2.3.14. Treatment of asbestos**

Waste contaminated with asbestos are actually landfilled in the EU, however new techniques are appearing in order to treat them prior to landfill disposal.

### **2.3.15. Bottom ash treatment**

#### **Purpose**

Improves the slag/bottom ash quality and therefore can help to improve its opportunities to be used as construction material.

Good bottom ash treatment facilities can produce a good quality material mainly scrap metal and mineral fractions. The residues from the treatment constitute 1 – 5 %. The residues are going back to the incineration. In addition, it is reduced the amount of heavy metals and e.g. arsenic (salt) that is emitted to the environment. Thus, the bottom ash treatment reduces the mass of waste to be landfilled.

#### **Principle of operation**

Bottom ash treatment plants exist in two types: wet and dry process.

#### **Feed and output streams**

Bottom ash from incinerators and other combustion processes.

### Process description

The following points describe some general measures which can be taken to help to improve the quality of slag for re-use after it has been generated (i.e. after the incineration and after the drying process). These include (no order is suggested with this list):

- separating the bottom ash from all other burning products, such as filter and boiler dust, with the intention to reduce the leaching possibilities of the waste (e.g. reducing leaching of heavy metals)
- avoiding mixing bottom ash from different sources
- removal of some of the organic material that it has not been entirely incinerated. Afterwards, incinerating this organic material removed. It is typically applicable when the waste OUT is used as a building material
- dewatering the bottom ash (it is commonly dried by storing it for a period of 2 - 4 weeks); this process requires a solid base (such as a concrete surface) and a collecting system for the effluent
- utilising a preliminary washing process to reduce the easily water soluble fraction of the bottom ash
- separating the scrap metal fraction from the bottom ash
- classifying and excluding the fine fraction from the bottom ash (the fine fraction is the most problematic fraction for the environment as it leaches out easily). Excluding the small fraction from the bottom ash leads to more landfilling, since there are no real alternatives for such fraction
- ageing the bottom ash. This improves the consistency and reduces adverse leaching effects. A ventilation system and an installed water circulation system can allow a better bottom ash quality
- analysing the eluate and the solids to assess the recovery possibilities of the material.

The ageing processes require a solid base and a collecting system for effluents. The common aging time is up to 3 months. The end of the ageing process is noticeable by specific temperature changes. The sieving, separation and wet preparation of the bottom ash are important steps to achieve a good result.

Two different types of bottom ash analysis are possible. The first method analyses the available mobile compounds (eluate analysis (i.e. leachate)) of the bottom ash fraction. The second method analyses the complete compounds of the bottom ash (solid analyses). It is common to use both methods in parallel to define the environmental effects of the bottom ash. However, the eluate analysis is more important with assessing the possibility of material recovery.

### Users

These techniques are seen by some Authorities as an important step to decrease the use of landfill. The amount of bottom ash from burning processes will rise, as probably the incineration of waste in Europe will become more common. Not only is the reduction of waste to disposal an environmental benefit, but it is also considered the re-use of the metal scrap fraction.

The wet process shows advantages concerning chloride-salts and final copper leaching, but is not compulsory in order to reach a bottom ash quality that allows re-use as a construction material in e.g. NL and DE.

## 2.4. Unit operations used in the physico-chemical processing of waste solids and sludges

This section contains common physico-chemical techniques used in the waste treatment sector. They are mainly common unit operations. They have been tabulated in Table 2.4, which gives the purpose and principle of the treatments and their main users.

Technique	Purpose and principle of operation	Users
Adsorption	See Table 2.3	

Technique	Purpose and principle of operation	Users
Centrifuging	See Table 2.3	Applied to liquid waste. Centrifuging is typically used together with recovery of the organic phase
Decanting	The principle of operation is the density difference of the different components to separate	Applied to liquid waste (e.g. separation of two immiscible liquids, recovery of liquid layers after separation of suspended solids or biological/chemical flocs)
Drying	Thermal drying as evaporation	Applied to contaminated soils, sludges
Extraction	See Table 2.3	
Filtration	See Table 2.3	
Flotation	See Table 2.3	Flotation is used on liquid waste when gravity settlement is not appropriate. It occurs when: <ul style="list-style-type: none"> <li>the density difference between the suspended particles and water is too low</li> <li>there is a space constraint at the site</li> <li>the waste contains oil or grease that needs to be removed before treatment</li> <li>recovery of the sludge is required</li> </ul>
Metal recovery		
Oil separation processes	See Table 2.3	Gravity separation of soluble oils and oil/water mixtures
Oxidation	See Table 2.3	The chemical oxidation of wastes is a well-established technology that is capable of destroying a wide range of organic molecules, including chlorinated organic carbons, VOCs, mercaptans, phenols, and inorganics such as cyanide. The most common oxidising agents used for hazardous waste treatments are ozone, hydrogen peroxide, and chlorine. Ultraviolet (UV) light is usually added along with ozone and/or hydrogen peroxide to accelerate the oxidation of chlorinated VOCs. It is a very common pretreatment operation at many plants, but has a variety of technologies
Scrubbing	Air scrubbing	
Sedimentation (settlement)	See Table 2.3	Applied to liquid waste. Sludges liberated from a settlement stage are typically around 1 % dry solids content
Stripping	See Table 2.3	<i>Air stripping</i> is one of the most commonly used processes for separation of waste water contaminated with VOCs, such as solvents. It can be used to remove the halogenated or non-halogenated hydrocarbons from dilute aqueous solution. Solutions high in ammonia can also undergo such pretreatment to reduce the concentration of ammonia. <i>Steam stripping</i> is utilised for the removal of volatile and sometimes semi-volatile compounds from waste water.

Technique	Purpose and principle of operation	Users
Supercritical treatments	Extraction and/or oxidation of pollutants from contaminated water or sediments. Supercritical fluids (e.g. carbon dioxide, water, ammonia, cyclohexane) are materials at elevated temperature and pressure that have properties between those of a gas and a liquid. In extraction, the organics in soils, sediment or water are dissolved in the fluid at elevated temperatures and pressure conditions and are then released from the extraction at lower temperatures and pressures. In supercritical water oxidation, air and contaminated water are brought together above the critical point of water and the complete oxidation of organic compounds occurs rapidly	Treatment of POPs
Water reactive chemicals pretreatment	These are scrubbed in a caustic solution and both treated liquors and scrubber liquors are treated in the main plant	The pretreatment of materials such as thionyl chloride, acetyl chloride, silicon tetrachloride with water to liberate acid gases
* The thermal treatments covered are those not included in the WI BREF		

**Table 2.4: Common unit operations used in physico-chemical treatments**  
[53, LaGrega, et al., 1994], [55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [150, TWG, 2004]

## 2.5. Physico-chemical treatments of other wastes

### Physico-chemical treatment of wastes containing POPs

Three ways have been identified for the destruction and irreversible transformation of the POP content in wastes [154, UNEP, 2004]. One is the incineration on land (not covered in this document but in the waste incineration BREF that also covers plasma techniques), another is the use of waste as fuel (e.g. co-incineration in cement kilns not covered in this document) and last one is the physico-chemical treatment of waste. This section concentrates on those physico-chemical treatments related to these very specific types of waste (e.g. waste containing PCBs, dioxins, furans) and they are summarised below in Table 2.5.

1. Technique	2. Principle of operation	3. Feed and output streams	4. Process description
5. Dechlorination with metallic alkali	6. Reaction of metallic alkali with chlorine atoms contained in the chlorinated compounds	7. Waste IN: PCB oils 8. 9. Waste OUT: organic compounds (oil which may be re-used) and salt	10. The dispersion is carried out at a temperature above that of the melting point of the sodium, i.e. 98 °C. Being liquid, the metal surface can be renewed continuously. In this way a reasonable reaction rate can be achieved, thus decreasing the cost of the decontamination process. 11. The process must avoid the formation of polymer (which occurs in one or two of the technologies identified) or must take the formation of this solid into account and introduce a separation step to yield the pure re-usable oil
12. Hydrogenation of POPs	13. Hydrogen reacts with chlorinated organic compounds or non-chlorinated organic contaminants, such as (PAHs), at high temperatures	14. Waste IN: transformer fluids; bulk PCB solids, including electrical capacitors; and high strength DDT waste pesticide mixtures 15. 16. Waste OUT: primarily methane and hydrogen chloride for PCBs and methane and minor amounts of light hydrocarbons for PAHs	17. Typical process used in mineral oil refineries and carried out at temperatures of 850 °C and higher. This technique converts approximately 40 % of the methane produced to hydrogen, via the water shift reaction, and the remaining part to hydrogen in the catalytic steam reformer. In this way, the process can operate without an external supply of hydrogen. For highly concentrated wastes, the process produces an excess of methane. It uses draw combustion air from off-site or ambient air on-site after first filtering it through active carbon, for the combustion process
18. Solvated electron process	19. Free electrons in a solvated electron solution convert contaminants to relatively harmless substances and salts	20. Waste IN: halogenated organic compounds, including PCBs, dioxins, pesticides, chlorofluorocarbons (CFCs) and chemical warfare agents. 21. 22. Waste OUT: decontaminated soils are said to be suitable for returning to the site, and as an additional benefit enriched in nitrogen from the trace amounts of residual ammonia	23. This technique uses an alkali or alkaline earth metal dissolved in a solvent such as ammonia, or certain amines or ethers to produce a solution containing free electrons and metal cations. Destruction efficiencies vary from 86 to 100 %. Chlorine and other halogens are selectively stripped from organic halides by free electrons and captured by the metal cations to form salts (e.g. CaCl <sub>2</sub> ). For example, a PCB molecule can be converted to biphenyl in a rapid reaction at ambient temperatures.
24. Supercritical water oxidation	25. A high temperature and pressure technique that uses the properties of supercritical water in the destruction of POPs	26. Waste IN: wastes containing organic compounds and toxic wastes 27. 28. Waste OUT: carbon dioxide; hydrogen to water; the chlorine atoms derived from chlorinated organic compounds to chloride ions; nitro-compounds to nitrates; sulphur to sulphates; and phosphorus to phosphate	29. Supercritical conditions
30. Note: Some other treatments outside the scope of this document are available for the treatment of wastes contaminated with POPs. These identified are co-incineration in cement kilns, hazardous waste incineration and plasma treatments			

**Table 2.5: Some specific treatments for waste containing PCBs and/or POPs**  
[100, UNEP, 2000], [154, UNEP, 2004]

### Physico-chemical treatments of CFCs

The aim is to treat the waste to transform the CFC in hydrochloric acid and hydrofluoric acid. An example of such plant is shown in Figure 2.5.

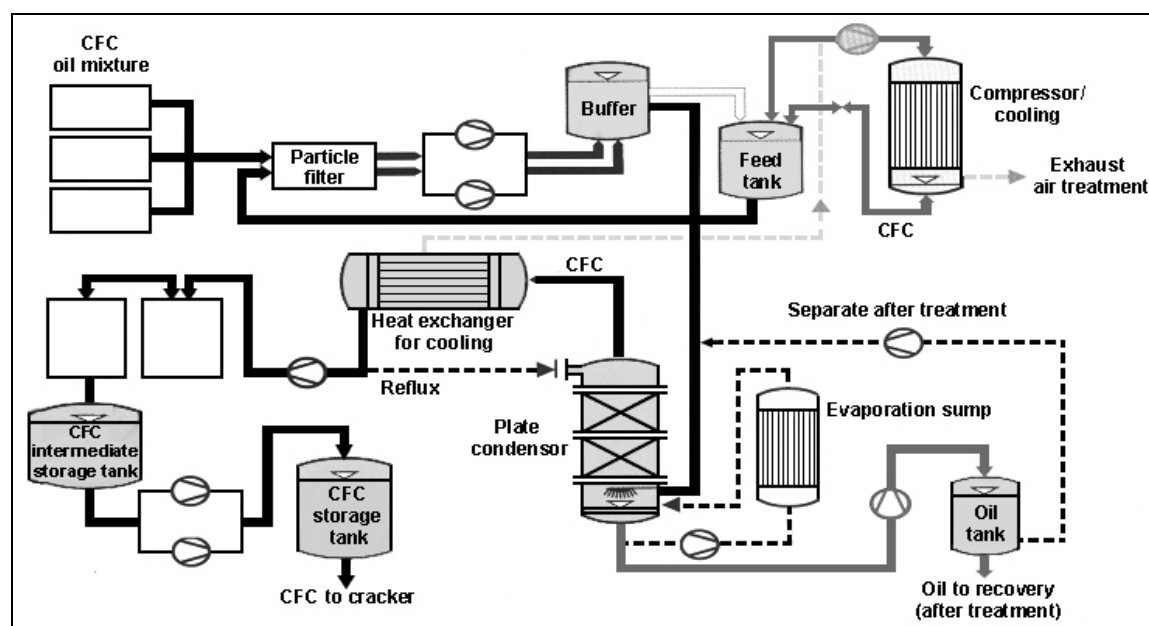


Figure 2.5: Treatment of CFCs to generate hydrochloric acid and hydrofluoric acid [150, TWG, 2004]

### Physico-chemical treatment of waste containing mercury

#### Purpose

The aim is to treat the waste to separate the mercury.

#### Principle of operation

In the process of vacuum distillation, waste containing mercury is evaporated under vacuum conditions at approximately 300 to 650 °C. The liquid components (e.g. mercury, water and oil) are distilled from the waste and condensed. In the condensation, a separation is established between the mercury and the distillate. The metallic mercury is drained and possibly refined. The mercury is recycled as a secondary raw material.

#### Feed and output streams

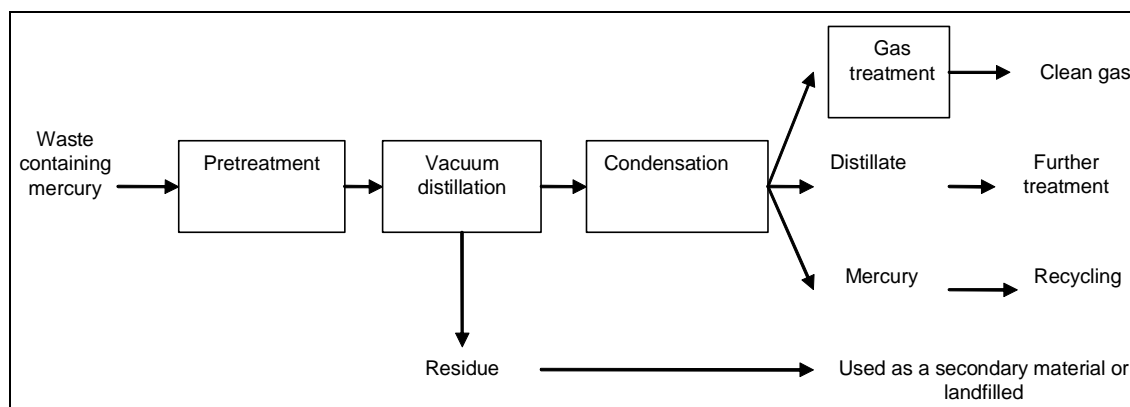
Sludge containing mercury from the oil and gas production industry, batteries, catalysts, activated carbon filters, thermometers, waste from the dental sector, fluorescent tubes, blasting grit and soil.

The destination of the residue from the vacuum vessel depends on the waste treated. It can be used as a secondary raw material (e.g. for batteries) or landfilled (e.g. in the case of sludge containing mercury).

#### Process description

The process is shown in Figure 2.6.





**Figure 2.6: Vacuum distillation of waste containing mercury**  
[156, VROM, 2004]

#### Users

Used in Sweden, Netherlands and Belgium.

### 3. Current consumption and emission levels

#### Emissions and consumptions from physico-chemical treatments

[30, Eklund, et al., 1997], [51, Inertec, et al., 2002], [55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [89, Germany, 2003], [94, USA DoE, 2002], [99, Fons-Esteve, et al., 2002], [100, UNEP, 2000], [101, Greenpeace, 1998], [121, Schmidt and Institute for environmental and waste management, 2002], [123, Perseo, 2003], [134, UBA, 2003], [147, UBA, 2003], [150, TWG, 2004], [152, TWG, 2004], [154, UNEP, 2004], [156, VROM, 2004], [157, UBA, 2004]

This section contains the emissions and consumptions of physico-chemical (Ph-c) treatments discussed in Section 0. Chemical treatment processes cover a wide range of unit operations and a wide range of wastes. This section also applies to chemical treatment plants operating neutralisation processes. The following sections highlight information available to site operators from their current record systems and the areas where emissions are likely to occur. Most sites are on a totally enclosed base with all liquids entering or generated on-site (including rainfall) returned to the process. This sector is very diverse, but also one of the best monitored sectors, as was observed in site visits.

The structure of each of the following sections in this section is the same as the one followed in Section 2.3. Emissions associated with an ancillary treatment, e.g. transfer station operation are covered in Section 3.1.

#### 3.1. Waste IN in physico-chemical treatments

##### Waste waters

The waste waters treated by physico-chemical treatments are:

- the core waste streams – these are inorganic acids and alkalis and their rinse-waters, together with cleaning, washing and interceptor wastes from a range of processes
- chemical industry wastes – these may include aqueous alcohol/glycol streams and process wash-waters
- (possibly) cleaning wastes with low levels of chlorinated compounds such as dichloromethane or phenolic compounds. Cleaning waters from the food industry may contain these substances as well
- aqueous wastes containing solvents
- high nitrogen wastes (potential for ammonia emissions)
- wastes containing phosphorus
- occasional inorganic wastes: for example wastes containing arsenic
- cyanide wastes - typically this waste will consist of solid or liquid cyanide salts, for example, sodium cyanide from surface metal treatments. They may also be present in printing wastes, usually as silver cyanide. Examples of cyanide based plating solutions include copper, zinc and cadmium cyanides
- developer waste (photographic wastes) typically includes a solution with a high percentage of ammonia salts, predominantly thiosulphate
- waste waters from shaping; oil wastes; organic chemical processes; and water and steam degreasing processes.

Without going into detail and/or individual and special cases, the essential sources of Ph-c plant treatable wastes are indicated in Table 3.1.

EWL chapter	Title	EWL list
-------------	-------	----------

06	Wastes from inorganic chemical processes	0601 waste acidic solutions 0602 waste alkaline solutions 0603 waste salts and their solutions 0604 waste containing metals 0605 sludges from on-site effluent treatment
07	Wastes from organic chemical processes	0701 wastes from the manufacture, formulation, supply and use (MFSU) of basic organic chemicals 0702 wastes from the MFSU of plastics, synthetic rubber and man-made fibres 0706 wastes from the MFSU of fats, grease, soaps, detergents, disinfectants and cosmetics
11	Inorganic wastes containing metal from metal treatment and the coating of metal; non-ferrous hydro-metallurgy	1101 liquid wastes and sludges from metal treatment and coating of metals (eg. galvanic processes, zinc coating processes, pickling processes, etching, phosphating, alkaline degreasing)
12	Wastes from shaping and surface treatment of metals and plastics	1201 wastes from shaping (including forging, welding, pressing, drawing, turning, cutting and filing) 1202 wastes from mechanical surface treatment processes (blasting, grinding, honing, lapping, polishing) 1203 wastes from water and steam degreasing processes
13	Oil wastes	1304 bilge oils 1305 oil/water separator contents
19	Wastes from waste treatment facilities, off-site waste water treatment plants and the water industry	1908 wastes from waste water treatment plants not otherwise specified

**Table 3.1: Types of waste that may be treated in a physico-chemical treatment plant [121, Schmidt and Institute for environmental and waste management, 2002]**

The essential mass flow from Ph-c plants is the waste water, corresponding to about 85 to 95 % mass of the waste accepted for treatment.

#### Aqueous marine waste

Most of the waste water from aqueous marine waste is contaminated with oil, organic substances and solid material (e.g. sediment). The contents of heavy metals, salts and other inorganic substances in the water and oil fractions are relatively low. Table 3.2 shows the acceptance and processing criteria for flocculation/flotation and biological treatment.

Component	Limit value acceptance (mg/l)	Limit value processing (mg/l)	List mixing policy*
PCBs	Detection limit	Detection limit	X
Dioxins	Detection limit	Detection limit	X
Pesticides	Detection limit	Detection limit	X
Organotin compounds	Detection limit	Detection limit	X
Brominated diphenyl ethers	Detection limit	Detection limit	X
Inhibition respiration	10 %	10 %	
N-total (Kjeldahl)	to discuss	500	
CN	to discuss	5	
Phenol	to discuss	1500	
VOX	100	20	
EOX	10	5	X
Cd	0.1	0.1	X
Hg	0.01	0.01	X
Total heavy metals	25	25	X

\*the limit value of acceptance is in accordance with the policy on mixing.

**Table 3.2: Acceptance and processing criteria for flocculation/flotation and biological treatment for aqueous marine waste**  
[156, VROM, 2004]

#### Waste solids and sludges

Some waste solids and sludges treated by physico-chemical treatments are:

- asbestos
- slag or bottom ash from combustion processes
- FGT waste (e.g. incineration ashes from MSW, hospital waste or industrial waste incinerators)
- sludge to be stabilised. Sludges from chemical industry may contain sulphates and organic salts
- stable waste
- sludge from waste water processing (municipal or industrial)
- residues from the metallurgical industry (dusts, sludge, slags). These may have high contents of Cr(VI)
- spent catalysts
- paint residues
- mineral residues from chemical processing
- wastes containing acid and soluble compounds
- high arsenic content residues from the chemical, metallurgical or ore industries
- contaminated soil. According to meeting devoted to assessing indicators for soil contamination [99, Fons-Esteve, et al., 2002], there are three main indicators used to establish whether soil is contaminated or not. These are typically acidification, eutrophication (the typical indicator is nitrogen content) and the content of heavy metals (e.g mercury). Contaminated soil can contain rocks, bricks, and reinforcing rods that could damage the equipment used for material handling if not removed.

The following text gives some information about some of these types of waste.

#### Bottom ash and FGT wastes from combustion processes

Some wastes from combustion processes are bottom ashes, FGT waste and filter cakes. Table 3.3 shows the physico-chemical characteristics of such waste from MSW incinerators:

Properties	Compounds	Values
pH		11 – 12.5 – 13
Soluble salts content	Cl, sulphates	Up to 70 % (Conductivity 15000 – 27000 –

		37000 $\mu\text{S}/\text{cm}$ )
Heavy metals	Pb, Zn, Cd, Cr	Up to several %
Inert compounds	Silica, alumina, lime	
Fine particulates		<100 $\mu\text{m}$
Density		Low (0.4 – 0.6)
Hygroscopic material	Salts, excess lime content	
Leaching test before treatment	Solubles Cr Cd Pb Zn As	10 – 80 % 1.5 – 8 ppm 1 – 500 ppm 1 – 1400 ppm 1 – 10000 ppm 1 – 50000 ppm
Middle number in ranges corresponds to averages.		

**Table 3.3: Characterisation of residues from MSW incinerators**  
[51, Inertec, et al., 2002]

The general components of slag/bottom ash from household incineration are silicates, alkaline earth, chloride, sulphates, non-ferrous metals (e.g. As, Cd, Cu, Pb), ferrous metals and heavy metals. The main components are the mineral fraction, the non-incinerated fraction and the scrap metal.

Categories	Percentage by weight (%)
Mineral fraction	85 – 90
Non-incinerated fraction	1 – 5
Metal scrap	7 – 10

**Table 3.4: Main components of slag/bottom ash**  
[89, Germany, 2003]

31. Values in %-wt	32. Slag/bottom ash (fresh)			33. Slag/bottom ash after storage 34. (ageing time of 3 months)		
35. Parameter	36. Min.	37. Average	38. Max.	39. Min.	40. Average	41. Max.
42. $\text{SiO}_2$	43. 42.91	44. 49.2	45. 64.84	46. 39.66	47. 49.2	48. 60.39
49. $\text{Fe}_2\text{O}_3$	50. 9.74	51. 12	52. 13.71	53. 8.41	54. 12.7	55. 17.81
56. $\text{CaO}$	57. 10.45	58. 15.3	59. 21.77	60. 10.42	61. 15.1	62. 23.27
63. $\text{K}_2\text{O}$	64. 0.83	65. 1.05	66. 1.36	67. 0.84	68. 0.91	69. 1.42
70. $\text{TiO}_2$	71. 0.65	72. 1.03	73. 1.33	74. 0.65	75. 0.88	76. 1.12
77. $\text{MnO}$	78. 0.06	79. 0.14	80. 0.22	81. 0.1	82. 0.17	83. 0.26
84. $\text{Al}_2\text{O}_3$	85. 6.58	86. 8.5	87. 10.79	88. 7.43	89. 8.83	90. 10.45
91. $\text{P}_2\text{O}_5$	92. 0.55	93. 0.91	94. 1.49	95. 0.5	96. 1.04	97. 2.61
98. $\text{MgO}$	99. 1.79	100. 2.69	101. 3.4	102. 1.84	103. 2.59	104. 3.51
105. $\text{Na}_2\text{O}$	106. 1.86	107. 4.3	108. 5.81	109. 2.05	110. 4.15	111. 7.49
112. Carbonates	113. 2.56	114. 5.91	115. 10.96	116. 5.59	117. 5.83	118. 7.62
119. Sulphates	120. 2.5	121. 15.3	122. 28.3	123. 5.8	124. 12.5	125. 22.5
126. $\text{Cl}$	127. 1.3	128. 3.01	129. 7	130. 1.5	131. 2.71	132. 4.6
133. $\text{Cr}$	134. 174	135. 648	136. 103	137. 295	138. 655	139. 1.6

(ppm)			5			17
140.Ni (ppm)	141.55	142.215	143.316	144.90	145.165	146.260 .2
147.Cu (ppm)	148.935	149.2151	150.624 0	151.124 5	152.2510	153.582 3
154.Zn (ppm)	155.1200	156.2383	157.400 1	158.179 5	159.3132	160.525 5
161.Pb (ppm)	162.497	163.1655	164.324 5	165.110 8	166.2245	167.390 0

**Table 3.5: Chemical composition of bottom ash after the household incineration plant [150, TWG, 2004]**

The following Table 3.6 and Table 3.7 describe some general values of bottom ash parameters after the incineration process, with data from two different treatment plants.

Values	Pb	Cr	Cu	Cd	As	Zn	Hg	Ni
Minimum	0.6	0.1	0.2	0.0001	0.003	0.5	0.07	
Average	1.6	0.5	2.2	0.021	0.012	4.8	0.7	
Maximum	5.2 – 6	2 – 9.6	7	0.02 – 0.08	0.022	10 – 21	2	0.5
Values in g/kg of bottom ash								

**Table 3.6: General bottom ash values after the household waste incineration process [89, Germany, 2003]**

Metal	Bottom ashes (slag) (ppm)	Bottom ashes <sup>1</sup> (slag) (ppm)	Fly ash and residues from dry and semi-dry processes (ppm) <sup>1</sup>	Mixture of fly ash and sludge from wet scrubbing process (ppm) <sup>1</sup>
Cd	0.3 – 70.5	0.01 – 0.1	1 – 10	<0.001
Cr	23 – 3170	0.001 – 0.01	1 – 10	0.01 – 0.1
Hg	0.02 – 7.75	0.001 – 0.01	<0.001	<0.001
Pb	98 – 13700	1 – 10	10000 – 100000	0.001 – 0.01
<sup>1</sup> Values correspond to concentration ranges in initial leachates Some more information on incinerators can be found in the waste incineration BREF				

**Table 3.7: Metals in bottom and fly ashes of municipal solid waste incinerators [113, COWI A/S, 2002], [150, TWG, 2004]**

During the combustion of coal, two types of coal ashes are generated. Classic fly ashes are mainly composed of non-combustible elements and non-burned particulates, and contain, on average, 50 % silica, 25 – 30 % alumina, 8 % iron oxides (containing Ca, K, Mg, Na, Ti and traces of As, Cd, Cr, Cu, Ni, Pb, Se, Zn). The other type of fly ash is composed of silico-calcareous ashes that are generated from the particulate abatement techniques and sulphur oxide abatement techniques. These ashes are rich in calcium sulphate. More information can be found in the Large Combustion Plant BREF.

The ashes from heavy fuel oil typically contain sulphur, vanadium and nickel. They are also characterised by high percentages of non-burned carbon, typically 60 % but can reach up to 80 %. More information can be found in the Large Combustion Plant BREF.

#### Asbestos

Table 3.8 below shows ranges found in the composition of different asbestos types.

Value in %	Friable asbestos	Transite asbestos
Al <sub>2</sub> O <sub>3</sub>	0.16 – 1.57	1.08 – 2.60
CaO	2.86 – 3.89	7.53 – 36.20
Fe <sub>2</sub> O <sub>3</sub>	5.43 – 8.17	0.55 – 11.85
FeO	0.00	0.00

<b>K<sub>2</sub>O</b>	0.02 – 0.26	0.39 – 0.43
<b>MgO</b>	69.00 - 78.49	1.22 – 56.13
<b>MnO</b>	0.04 – 0.18	0.01 – 0.2
<b>Na<sub>2</sub>O</b>	0.41 – 0.73	0.01 – 0.14
<b>P<sub>2</sub>O<sub>5</sub></b>	0.16 – 0.22	0.02 – 0.20
<b>SiO<sub>2</sub></b>	12.04 – 16.10	20.87 - 60.01
<b>TiO<sub>2</sub></b>	0.02 – 0.06	0.09 – 0.23
<b>Loss on ignition <sup>1</sup></b>	48.47 – 51.53	17.96 – 44.35
<sup>1</sup> Indicator of the organic content of the sample.		

**Table 3.8: Asbestos composition**  
[94, USA DoE, 2002]

#### High temperature drying

The drying facility performs the pretreatment of aqueous paste-like wastes such as metal hydroxide sludges or coagulated lacquer and paint sludges.

#### Thermal distillative drying

Solid/paste like hazardous wastes which contain considerable amounts of free or bound fluids are treated. They are processed in order to recover solvents, to produce defined solid products or for drying in the facility.

In addition, heat cost allocator tubes or aerosol cans may also be treated. Heat cost allocator tubes are used for measuring heat energy consumption. They consist mainly of a glass tube and methyl benzoate as the evaporative medium. The drying residue (cullet) of the heat cost allocator tubes can be smelted in the corresponding steel mills or used in road construction. The condensate from the drying process can be recycled, i.e. it is re-used for the production of heat cost allocator tubes.

#### **Waste IN in the treatment of specific wastes**

##### Hydrogenation of POPs

According to the US DOE, this system can handle most types of waste, including landfill leachates, lagoon bottoms, soils, sludges, liquids, and gases. However, US DOE has cautioned that reaction by-products and intermediate reduction products need to be monitored in the off-gas from both the reduction process and the boiler. US DOE also noted the need to determine the fate of mercury and other volatile inorganics.

The process is non-discriminatory; that is organic molecules such as PCBs, PAHs, chlorophenols, dioxins, chlorobenzenes, pesticides, herbicides and insecticides are quantitatively converted to methane.

##### Supercritical water oxidation

Environment Australia reports that technology is limited to the treatment of waste that is either liquid or that has a particle size of less than 200 µm, and it is most applicable to wastes with an organic content of less than 20 %.

Supercritical water oxidation has been applied to a broad range of materials, e.g. aqueous waste streams, sludges, contaminated soils, industrial organic chemicals, plastics, synthetics, paints and allied products, industrial organics, agricultural chemicals, explosives, petroleum and coal products, and rubber and plastic products. It is applicable to the treatment of a range of contaminants including acrylonitrile waste water, cyanide waste water, pesticide waste water, PCBs, halogenated aliphatics and aromatics, aromatic hydrocarbons, MEK and organic nitrogen compounds.

##### The solvated electron technique

Table 3.9 below shows the waste IN and waste OUT for the treatment of chlorinated waste by the solvated electron technique.

<b>Material treated</b>	<b>Products</b>	<b>Disposal options</b>
Concentrated PCBs	Biphenyl, Ca(OH) <sub>2</sub> , CaCl <sub>2</sub>	Landfill as salts
PCBs in soils	Biphenyl, Ca(OH) <sub>2</sub> , CaCl <sub>2</sub> , clean soil	Return soil to ground
PCBs on surfaces	Biphenyl, Ca(OH) <sub>2</sub> , CaCl <sub>2</sub>	Collect salts and landfill

PCB/oil mixtures	Biphenyl, Ca(OH) <sub>2</sub> , CaCl <sub>2</sub> , oil	Re-use oil. Landfill salts
Concentrated HCB	Benzene, NaCl, NaOH.	Separate benzene and landfill salts
HCB in soils	Benzene, NaCl, NaOH, clean soil	Separate benzene and return soil with salt to ground

**Table 3.9: Products and disposal options for the use of solvated electron technique**  
[100, UNEP, 2000]

### 3.2. Consumptions of physico-chemical treatments

#### Waste waters

In some physico-chemical treatments, bases are necessary. In some cases, waste bases are re-used in waste applications for neutralisation purposes. The neutralising agent used could be a solid or liquid waste stream or a bought-in alkali, as most plants need to buy in some supplementary alkalis. Aqueous acid containing metals, alkali and neutral wastes are common additions and the Ph-c plants are typically designed to produce a sludge containing slightly alkaline metal. Table 3.10 shows the consumptions of some physico-chemical treatments of contaminated water.





Parameter	Yearly consumption (t/yr) *	Specific consumption (kg/tonne of waste treated) *	Yearly consumption in inorganic pathway (t/yr)	Yearly consumption in organic pathway (t/yr)	Yearly consumption of WWT (t/yr)	Yearly consumption of lacquer treatment facility (t/yr)	Yearly consumption of laboratory chemical treatment (t/yr)
Average throughput	45000		20000	66000	30000	Lacquer: 15000 Solvent: 15000 Lacquer powder: 1000	1000
Average consumption of acids	230 <sup>1</sup>	5.1	HCl: 69 Sulphuric: 48	HCl: 8 Phosphoric: 8	HCl: 39.4		0.5
Lime	590 <sup>1</sup>	13.1	1023		50		10
Flocculation agents	290	6.4		8	16		
Other chemicals <sup>2</sup>		0.4 – 3.0					
Sodium sulphite			10.2		2		
Water consumption			759	9900	1788	2700	
Energy consumption				275 kW	369 MWh	Fuel oil: 1139 m <sup>3</sup> Electricity: 189 MWh	
Waste water			11573	48348	12687		250
Hydrogen peroxide			6.2				0.1
Sodium hypochlorite			4.9				
Iron chloride solution				118			
Iron oxide					65.8		
Sodium hydroxide				110			1
Activated carbon				6			
Potassium permanganate					0.4		
Splitting additives					25		
Amidosulphone acid					n.a.		
<p>* Notes: Data based on the data from Ph-c plant operators with a capacity of 850 kt/yr combined. The data correspond to year 2001. The average age of the plants is about 17 years (ranging from 4 to 39 years). Approximately 84 % (from 73 to 91 %) of all the Ph-c plants for treatment of accepted waste observed here, can be attributed to EWL groups 11,12,13,16 and 19</p> <p><sup>1</sup> Values do not include waste acids or waste alkalis accepted and used</p> <p><sup>2</sup> Detoxification chemicals, organic breaking up of emulsions, sorption, sulphuric precipitation</p>							

**Table 3.10: Consumptions of physico-chemical treatment of waste waters**  
**[121, Schmidt and Institute for environmental and waste management, 2002], [135, UBA, 2003]**

A total amount of approximately 0.4 m<sup>3</sup> prepared chemicals are used per m<sup>3</sup> waste water. Table 3.11 shows the chemicals consumed and some of their consumption levels for detoxification, neutralisation and dewatering for the removal of metals.

168. Chemical	169. Consumption
170. Lime or sodium hydroxide for neutralisation/precipitation	171. (NaOH 50 %) 120 l/m <sup>3</sup> waste water
172. Sulphuric or hydrochloric acid for acidification	173. (HCl 30 %) 10 l/m <sup>3</sup> waste water
174. Hypochlorite (oxidation cyanide)	175.
176. Iron (II) sulphate or sodium bisulphite (reduction Cr <sup>6+</sup> to Cr <sup>3+</sup> )	177.
178. Aluminium sulphate or chloride (flocculation)	179.
180. Iron (III) chloride (flocculation)	181.
182. Sodium sulphide (precipitation)	183. 0.3 kg/m <sup>3</sup> waste water
184. Materials for the improvement of precipitation, flocculation, coagulation and complex destruction	185.

**Table 3.11: Chemicals consumed and some of its consumption levels for detoxification, neutralisation and dewatering for the removal of metals from waste waters [156, VROM, 2004]**

#### Precipitation/flocculation

The following inorganic materials are predominantly used in precipitation/flocculation:

- caustic soda
- soda ash (sodium carbonate)
- lime
- iron (III) chloride
- iron (II) chloride
- aluminium sulphate
- sulphides.

Synthetic flocculation materials are also used for the improvement of floc formation and sedimentation characteristics. They consist principally of non-ionic polymers, anionic polymers, cationic polymers and co-polymers of ionic and non-ionic compounds.

Table 3.12 shows the chemicals used for the precipitation of solute heavy metals; this information refers to chemically pure chemicals. In practice, it may be seen that the quantities actually required may be 10 to 20 % larger. Precipitation values for different metals are shown in Table 3.13.

Used alkali (g)	Metal to be precipitated					
	Fe (II)	Fe (III)	Cu	Ni	Cr	Zn
CaO	100	150	88	96	162	86
Ca(OH) <sub>2</sub>	134	201	116	126	213	114
NaOH	144	216	126	136	231	122
Na <sub>2</sub> CO <sub>3</sub>	190	285	168	181	307	162
MgO	73	110	63	69	117	62
Mg(OH) <sub>2</sub>	105	158	92	100	169	90

**Table 3.12: Theoretical consumption of alkalis in precipitation per 100g metal [121, Schmidt and Institute for environmental and waste management, 2002]**

Limit values pH	3	4	5	6	7	8	9	10	11	12
Pb <sup>2+</sup> <0.5 mg/l										
Cd <sup>2+</sup> <0.2 mg/l										
Ni <sup>2+</sup> <0.5 mg/l										
Zn <sup>2+</sup> <2.0 mg/l										
Fe <sup>2+</sup> <3.0 mg/l										
Cu <sup>2+</sup> <0.5 mg/l										
Cr <sup>3+</sup> <0.5 mg/l										
Al <sup>3+</sup> <3.0 mg/l										
Sn <sup>2+</sup> <2.0 mg/l										
Fe <sup>3+</sup> <3.0 mg/l										
pH	3	4	5	6	7	8	9	10	11	12

	pH ranges, with which the solubility of the metal hydroxide precipitation with caustic soda solution lies below the values mentioned in the first column
	Expansion of these ranges through the use of lime milk
	Expansion of these ranges through the use of soda

**Table 3.13: Range of precipitation values for various metals**  
**[121, Schmidt and Institute for environmental and waste management, 2002]**

Precipitation sludge must be disposed of if recycling is not possible. Dewatering is generally necessary. Precipitation/flocculation materials must be selected to suit the dewatering procedure used. Sludge formed from materials containing aluminium generally display poor dewatering characteristics.

Precipitation/flocculation is a reaction and/or a reaction combination which is essentially dependent on the pH value. To this extent, the most significant reference parameter is the pH value. Since the waste water produced through precipitation/flocculation is discharged into sewerage systems, certain criteria must be met. In order to maintain these values, additional treatment steps and procedures for the treatment of waste water follow flocculation and precipitation.

### Oxidation/reduction

Redox reaction	Oxidant or reductor	pH	Observations
Oxidation of cyanide and nitrite	Sodium hypochlorite (NaOCl) or chlor gas (Cl <sub>2</sub> )	for CN: ~ 10 for NO <sub>2</sub> : ~ 3	<ul style="list-style-type: none"><li>• reaction relatively quick</li><li>• relatively high degree of salting up of the resultant waste water</li><li>• formation of organic materials, which are shown as AOX (Note: the limit value is AOX = 1 mg/l in the waste water to be introduced into the sewerage system)</li></ul>
Oxidation of cyanide and nitrite	Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	for CN: ~ 10, catalyst: Fe (II)-salts for NO <sub>2</sub> : ~ 4	<ul style="list-style-type: none"><li>• reaction relatively slow</li><li>• negligible salting up of the waste water,</li><li>• no new formation of materials as AOX</li><li>• formation of mud, due to catalyst (Fe II-salts)</li><li>• formation of foam (in particular in the presence of organic materials)</li></ul>
Oxidation of nitrite	Aminosulphonic acid (NH <sub>2</sub> SO <sub>3</sub> H)	~ 4	<ul style="list-style-type: none"><li>• reaction slowed</li><li>• formation of sulphates</li><li>• formation of elementary nitrogen</li></ul>
Reduction of chromate	Sodium hydrogen sulphite (NaHSO <sub>3</sub> )	~ 2	<ul style="list-style-type: none"><li>• fast reaction</li><li>• causes salting up of the waste water</li><li>• formation of mud</li></ul>
Reduction of chromate	sulphur dioxide (SO <sub>2</sub> )	~ 2	<ul style="list-style-type: none"><li>• fast reaction</li><li>• slight salting of the waste water</li><li>• slight mud formation</li></ul>
Reduction of chromate	Sodium dithionite (Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> )	pH independent	<ul style="list-style-type: none"><li>• fast reaction</li><li>• leads to salting of the waste water</li><li>• formation of mud</li></ul>
Reduction of chromate	Iron (II) sulphate or chloride (FeSO <sub>4</sub> /FeCl <sub>2</sub> )	~ 3	<ul style="list-style-type: none"><li>• slow reaction</li><li>• leads to the salting up of the waste water</li><li>• formation of mud</li></ul>

**Table 3.14: Consumption of chemicals for redox reactions**  
[121, Schmidt and Institute for environmental and waste management, 2002]

### Sorption (adsorption/absorption)

Table 3.15 contains information on various adsorbencies. The large area of activated carbon, which according to this is particularly well suited for the adsorption of materials is notable. However it must then be ensured that the material to be adsorbed (i.e. to be separated) also reaches the inner surface of the activated carbon. It is therefore the essential task of the reactor and plant technology to achieve an intensive contact between the material and the adsorbent to be separated. In the treatment of material mixtures, the effect and/or efficiency of adsorbents is determined in general by experiment.

TYPE	Characteristics			
	Specific surface (m <sup>2</sup> /g)	Micropore volumes (ml/g)	Macropore volume (ml/g)	Apparent weight (g/l)
Grain carbon for water purification	500 – 800	0.3 – 0.6	0.3 – 0.4	300 – 500
Powder carbon for decolourisation	700 – 1400	0.45 – 1.2	0.5 – 1.9	250 – 500
Fine-pore silica gel	600 – 850	0.35 – 0.45	<0.1	700 – 800
Large-pore silica gel	250 – 350	0.3 – 0.45	0.05 – 0.1	400 – 800
Activated alumina	300 – 350	0.4	approx. 0.1	700 – 800
Adsorbent resin	400 – 500			650 – 700

**Table 3.15: Physical data of adsorbents**  
[121, Schmidt and Institute for environmental and waste management, 2002]

#### Ion exchangers

Ion exchangers	Stability		Regeneration substance g/l resin
	pH	°C	
Weak-acid, cation exchanger ionic form: H <sup>+</sup> , PF <sup>+</sup>	1 - 14	75 - 120	HCl: 70 – 140 or H <sub>2</sub> SO <sub>4</sub>
Strong acid, cation exchanger ionic form: H <sup>+</sup>	1 - 14	~120	HCl: ~80
Weak base, anion exchangers ionic form: OH <sup>-</sup> , Cl <sup>-</sup>	1 - 14	70 - 100	NaOH: ~60
Strong base, anion exchangers ionic form: OH <sup>-</sup> , Cl <sup>-</sup>	1 - 12	35 - 70	NaOH: ~80

**Table 3.16: Overview of types of exchangers and their properties**  
[121, Schmidt and Institute for environmental and waste management, 2002]

#### Aqueous marine waste

Heat is required for the heating of tanks and pipelines in order to keep them frost-free, for the preparation of chemicals, for the improvement of separation processes and for other processes. The amount of energy consumed depends on climatic conditions. Electricity is required for pumps, compressors and other facilities. Further differences in energy consumption may be caused by a difference in storage capacity or the application of evaporation.

The overall consumption of energy for heat production varies from 140 to 490 MJ/m<sup>3</sup> waste water. The overall consumption of electricity varies from 65 to 170 MJ/m<sup>3</sup> waste water. The energy data include other activities such as the cleaning of vessels, which means that they are an overestimate of the energy consumption needed for physico-chemical and biological treatment.

For several steps in the treatment, chemicals are used, e.g. alkalis, acids, flocculating and coagulating agents, activated carbon and oxygen. The use of waste acids and alkalis reduces the consumption of primary chemicals. In Table 3.17, some data on the consumption of chemicals are presented.

Chemical	Consumption (kg/m <sup>3</sup> waste water)	Comments
Alkalis	2 – 3	
Acids	0 – 1	Depends on the use of waste acids
Flocculating/coagulating agents	1 – 7	
Oxygen	5	Depends on the use of air or oxygen
Activated carbon	0.04	

**Table 3.17: Data on consumption of chemicals in the treatment of aqueous marine waste and similar waste [156, VROM, 2004]**

Water is required in centrifuges and for the preparation of chemicals. The use of the effluent from the biological treatment reduces the consumption of water.

#### **Waste solids and sludges**

Table 3.18 and Table 3.19 show consumption values from soil washing treatment plants.

Consumption	Used for	Value
Electrical	Pumps and attrition units	15 – 25 kWh per processed tonne of soil
Chemical	Function of the treated pollution. Some chemicals (such as the flocculating agents) are usually used in all plants	3 to 5 kg per tonne of dry sludge
Water	Mainly due to loss of water with the residual filter cake	0.1 to 0.3 tonnes per tonne of processed soil

**Table 3.18: Consumptions of soil washing processes plants [123, Perseo, 2003]**

186.Capacity	187.t/yr	188.68000
189.Fuel consumption	190.MJ/yr	191.0
192.Electricity consumption	193.MWh/yr	194.900
195.Electricity/plant capacity	196.kWh/t	197.13.235
198.Heat consumption	199.MWh/yr	200.0
201.Cooling	202.MJ/yr	203.0
204.Chemicals	205.sodium hydroxide 206.anti-foaming products 207.polyelectrolyte	

**Table 3.19: Consumptions of a installation treating contaminated soil by washing [66, TWG, 2003]**

### **3.3. Emissions from physico-chemical treatments**

#### **3.3.1. Emissions from the physico-chemical treatments of waste waters**

The physico-chemical treatment of waste waters generates a flow of decontaminated water which corresponds to the so-called waste OUT stream of the treatment. An analysis of this stream is given in Section 3.4. The following two figures (Figure 3.1 and Figure 3.2) extrapolate flow diagrams leading to the emissions from the physico-chemical treatment of waste waters.

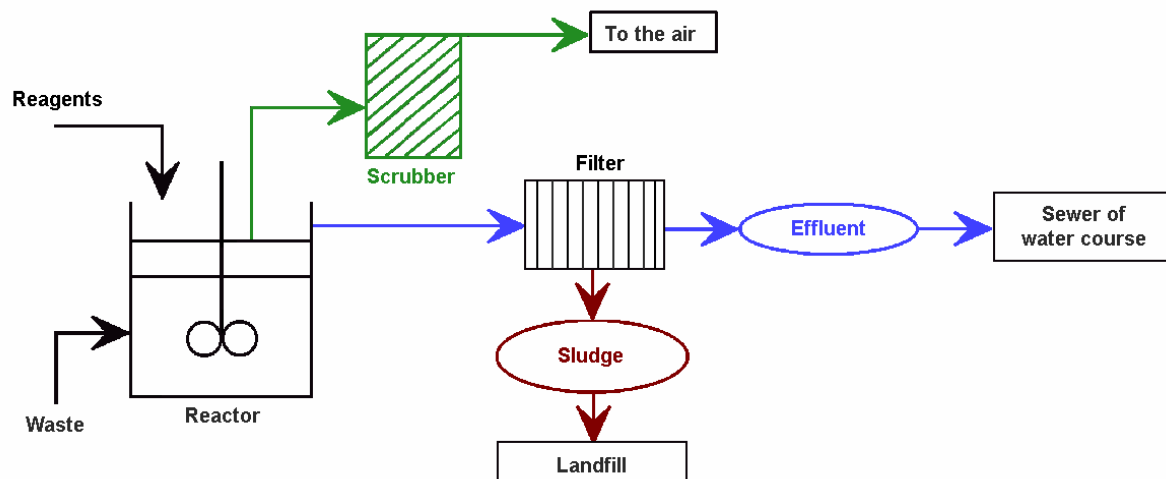


Figure 3.1: Main emission flows from the physico-chemical treatments of waste water [80, Petts and Eduljee, 1994]

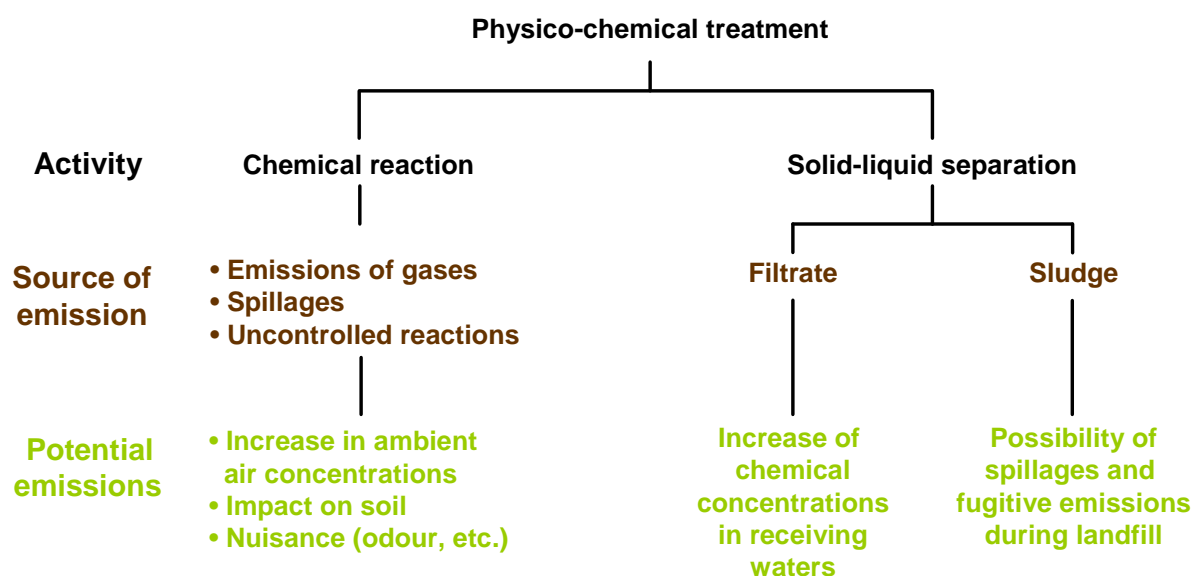


Figure 3.2: Potential emission streams from physico-chemical treatments

Note: Some of these emissions only appear in badly operated physico-chemical treatments [80, Petts and Eduljee, 1994], [150, TWG, 2004]

#### Air emissions

Some organic compounds can travel through the plant without being removed and then end up in the final sludge or effluent, whereas others may be evaporated during the exothermic reactions of neutralisation or during sludge pressing. Certain organic wastes contain 'hidden' species. For example, lubricating oils contain



naphthalene, BTEX, phenols, copper and nitrogen and can lead to ammonia and xylene emissions to the air during the oil separation from water, or to increased levels in the final site effluent. Aqueous wastes containing solvents may be emitted due to the heat of the process. High nitrogen wastes have a potential for ammonia emissions to the air.

Some materials passing through the plant (typically not captured by physico-chemical processes) are TOC/COD, dichloromethane, phenol, BTEX and naphthalene associated with the waste water from oil pretreatment and TOC, dichloromethane, phenol, BTEX and naphthalene associated with the waste from oil pretreatment.

The air emissions from individual plants depends on the abatement system used. Very few plants have monitoring programmes in place that can quantify their air emissions. Air emissions from these treatments are typically VOCs, acid gases and ammonia. Although difficult to quantify given the lack of monitoring programmes, it can be seen that if closed treatment vessels and air collection/treatment systems are in use, these emissions are reduced. Issues such as the presence of low concentrations of organic solvents in the waste might not always be picked up by WT operators, but these may be important environmentally as they could lead to relevant emissions to the air during the process.

Air emissions may be associated with rapid pH changes, rapid temperature rises and with vigorous agitation. Gaseous reaction products also still occur. Most installations will liberate VOCs from the waste through a mixture of heating, agitation or sludge pressing or drying. There is also always a possibility that reaction intermediates may be released as well. Emissions of metals to the air can be assessed on analytical results. Evaporation also occurs in an uncontrolled manner, such as the evaporation of solvents when mixing solids and liquids or from the stirring of sludges in open tanks.

Emissions of organic compounds may appear when treating mixed waste streams (for example, from the neutralisation of acid, solvents are displaced into the vapour phase which cannot be abated by a wet scrubber used to abate acidic emissions) or are present because its recovery is neither technically nor economically viable (that is, as contaminants associated with wastes that are difficult to handle are treated by other methods).

Air emission parameters	Measured annual average emission values (mg/Nm <sup>3</sup> )	Mass flow (g/h)
Flow of exhaust air	325 Nm <sup>3</sup> /t	
TOC <sup>1</sup>	2.84 – 36	500 (534 kg/yr)
Dust	0.21	40.3 kg/yr
BTX	4.9	
Benzene		2.5
HCN	<0.05 – 0.12	0.043 - 15
H <sub>2</sub> S	0.31	15
Cl <sub>2</sub>	<0.03	15
SO <sub>2</sub>	1.17	0.5
HCl	0.3	0.2
Hg	0.01	0.0034
Notes: Data based on the data from Ph-c plant operators with a total capacity of 850 kt/yr. The data correspond to year 2001. The average age of the plants is about 17 years (ranging from 4 to 39 years). Approximately 84 % (from 73 to 91 %) of all the Ph-c plants for the treatment of accepted waste covered here can be attributed to EWL groups 11,12,13,16 and 19. Exhaust air emissions are in general measured intermittently. The measurements are essentially made to monitor the processes, where contamination of the exhaust air can be expected in the intended operation, such as evaporation or cyanide oxidation. <sup>1</sup> Values correspond to mg of carbon		

**Table 3.20: Air emissions from physico-chemical treatment of waste water**

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[121, Schmidt and Institute for environmental and waste management, 2002], [135, UBA, 2003], [157, UBA, 2004]

The emissions of VOC from aqueous marine waste treatments range from 0.4 to 0.6 kg/m<sup>3</sup> waste water if no exhaust gas treatment is applied. Biological treatment generates emissions of odour. One of the example plants reports an average emission level of 540 million ouE/h.

#### **Water emissions (for more information see Section 3.4)**

Aqueous residues (if any) are generally sent to sewer. Wastes from the chemical industry, high nitrogen wastes (maybe landfill leachates) and oil recovery/re-processing may introduce additional species and thus need to be considered more carefully. High nitrogen wastes increase the likelihood of a discharge of nitrous oxide. Metals, ammonia and organic chemicals are typically present in water streams.

In all cases, the effluent consents will require protection of the sewerage treatment works from the plant discharge, this protection is focused on COD, pH, oil content, ammoniacal nitrogen, metal content, sulphates and sulphides, as well as dichloromethane (the most common halogenated cleaning compound and liable to be a contaminant of wash-waters and interceptors). The total discharge volume will usually be known.

Although precipitation techniques for metals are reasonably effective, a typical physico-chemical process (under a trade effluent consent) may discharge between 1 – 3 tonnes of metals to sewer annually (the actual value depends on the size of the plant and the amount and type of waste. For example, considering the emission values that appear in Table 3.34, and without considering Fe as a metal, a volume of waste water of 500000 m<sup>3</sup> is necessary to reach some of the upper levels of the range). This is associated with particulates carried over in the effluent from the process and arising from inefficiencies in either the precipitation stage or during settling out of the precipitated metals.

Most sites do not have data for the chloride, total nitrogen and total phosphorus in the sewer discharge. Rough calculations show that for sites where data are available, the emissions are low, unless the site specialises in phosphoric acid treatment or handles high nitrogen flows. Most sites are required to analyse for ammoniacal nitrogen so they can provide a minimum emission value.

The process of waste waters mixed with organic material (e.g. mix of mineral oil, synthetic oil, kerosene, interceptor waste, aliphatic hydrocarbon, aromatic hydrocarbon, alcohol, chlorinated solvents, esters, ethers, aldehydes, ketones, fats, waxes, greases) generates around 836 kg of waste water per tonne of waste IN and 5.5 kg of sludge per tonne of waste IN.

Emissions to water of salts, e.g. sulphates and chlorides, occur. These salts are added as reagents and are not removed in the process of precipitation, neutralisation and filtration. This causes the effluent to have high concentrations of these compounds.

#### **Solid wastes and emissions to land**

The sludge generated from physico-chemical treatment plants can be pressed and sent to further treatment, pressed and mixed with other sludges (generally organic) on site or mixed with residues from flue-gas cleaning to give a solid product (with exothermic reaction). Almost all of the sites produce a sludge/cake, which is then commonly incinerated or co-incinerated, or in a few cases directly landfilled.

Metal levels in the waste are well characterised, but organic contamination is not. N and P are not typically quantified in waste and will be present in the aqueous solution.

Process generated waste	Specific amount (kg/tonne of total waste processed in the Ph-c treatment plant)
Oil	30 – 90
Concentrates <sup>1</sup>	14 – 40
Hydroxide sludge <sup>2</sup>	60 – 90

Mud from purification and emptying processes	10 – 50
<p>Notes: Data based on the data from Ph-c plant operators with a total capacity of 850 kt/yr. The data correspond to year 2001. The average age of the plants is about 17 years (ranging from 4 to 39 years). Approximately 84 % (from 73 to 91 %) of all the Ph-c plants for the treatment of accepted waste observed here, can be attributed to EWL groups 11,12,13,16 and 19.</p> <p>The oil is generally recycled and the remaining substances recycled or disposed of, depending on their characteristics and the market conditions.</p> <p><sup>1</sup> Concentrates from evaporation/stripping and membrane filtration as well as from ultrafiltration and ion exchangers.</p> <p><sup>2</sup> The weight relates to damp mud, drained TS: ~35 – 45 %.</p>	

**Table 3.21: Process generated waste from physico-chemical treatment plants**  
[121, Schmidt and Institute for environmental and waste management, 2002]

Waste from the Ph-c treatments arise principally from precipitation/flocculation, concentrates from membrane filtration, evaporation or ion exchange; waste is also produced in cleaning and draining processes, constructions and containers. The extent to which waste can be used depends on the individual case. For example, separated oil is generally recyclable, concentrates from membrane filtration, evaporation or ion exchange can be recycled in some cases, sludge from precipitation/flocculation are generally disposed of, waste from cleaning and draining are generally disposed of and disposal is usually by immobilisation or incineration.

Table 3.22 below shows the composition of sludge generated in the physico-chemical treatment of waste waters.

Compound	Value	Unit
pH	7 – 9	
TOC	54.7	wt-%
Loss of ignition	54.7	wt-%
Hydrocarbons	30000	mg/kg
PCDD/F	<0.1	ng-TE/kg
PCB ( $\Sigma$ 6)	<0.12	mg/kg
EOX	10	mg/kg
CN total	<0.1	mg/kg
As	0.2	mg/kg
Cd	2.7	mg/kg
Cr total	887	mg/kg
Cu	349	mg/kg
Hg	0.2	mg/kg
Ni	210	mg/kg
Pb	211	mg/kg
Tl	14	mg/kg
Zn	1970	mg/kg

**Table 3.22: Sludge generated in the physico-chemical treatment of waste waters**  
[157, UBA, 2004]

The amount of sludge containing metal (filter cake) that is produced depends on the specific contaminants in the waste water, their concentrations and on the reagents and other chemicals that are used. The sludge quantity varies from 2.5 to 10 % of the waste water input. By replacing lime by sodium hydroxide the amount of filter cake is reduced. However, lime is necessary for the precipitation of fluorides.

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The filter cake with high concentrations of metals, e.g. nickel and copper, can be used as a raw material in the metallurgical industry. In other cases, the filter cake is disposed of as solid waste.

Solid residues from aqueous marine waste

The generated solid residues are:

- solid residues from the decanter/centrifuge and filters (50 kg/t waste water)
- separated oil and chemical fractions (possibly suitable for re-use as fuel).

**Emissions from particular physico-chemical activities**

The emissions listed in Table 3.23 below can be expected to occur from most treatment plants. The scale of the emission depends on the plant throughput and on the abatement systems applied.

NON OFFICIAL FEAD VERSION

Physico-chemical activity	Air	Water	Residues/Soil
Addition of solid sodium carbonate or addition of sulphuric acid to form nickel or chromium sulphate	Emissions of CO <sub>2</sub> , plus other acid gases (e.g. SO <sub>x</sub> ) depending upon the initial solutions	Liquid fraction is returned into the treatment and blending part of the plant. This is a tiny fraction of the main waste IN	The product precipitates out and is left to cool and crystallise before being bagged and sent off for recycling
Cyanide oxidation		HOCl	
Fluorescent tubes/lamp processing	Hg and SO <sub>x</sub>	The discharge is a weak sodium hydroxide solution	
Precipitation of metals		Zn, Cu, Cd	
Silver recovery systems	There is an unquantified issue of ammonia, and possibly SO <sub>x</sub> , from photographic chemicals due to the high nitrogen and sulphur levels in the solutions. Additionally there may be There are additional VOC emissions due to bulking and transfer processes		Possibly high nitrogen levels in the waste
Treatment of printing and photographic waste	Ammonia, VOC and potentially SO <sub>x</sub>	Suspended solids, nitrogen (mainly nitrate) and COD	Waste typically has a high nitrogen content
Use of raw caustic		Hg	
<i>Unit operations</i>			
Air stripping	Ammonia and VOCs, including organic solvents (e.g. DCM)		
Dissolved air flotation (DAF)			Sludges that are taken from the bottom of settlement tanks will generally be up to 4 % dry solids
Evaporation	Normally takes place in fully enclosed systems but various vent valves can result in fugitive emissions		
Filtration/pressing This is a common area for emissions from chemical plants	Ammonia and, if there is a high organic content in the wastestreams, VOCs		
Ion exchanger		The eluate of an ion exchanger must be further treated in the plant according to its composition/concentration	

Physico-chemical activity	Air	Water	Residues/Soil
Mixing tanks	May produce a range of emissions, partly as the result of chemical reactions, and partly from heat effects reducing the solubility of gases in water. Ammonia is the most common gas mentioned as a problem at this stage of the process.		
Neutralisation	This can be a violent exothermic reaction with a rapid change in pH. Acidic acids such as CO <sub>2</sub> , HCl, Cl <sub>2</sub> , NO <sub>x</sub> , and SO <sub>x</sub> , as well as ammonia are emitted from the reactor tank, together with any contaminant volatile materials, such as cleaning solvents in wash-waters. The gases can carry liquors and particulate matter with them	Typical components are chloride, phosphorus, nitrogen and metals	Typical components are chloride, phosphorus, nitrogen and metals
Organic splitting of emulsions			Generally smaller quantities of mud (filter cakes) develop in organic splitting than with acid splitting
Oxidation/reduction		The salination of the waste water is process-dependent	
Settlement	Emissions to the air are possible but unlikely		Sludges that are taken from the bottom of settlement tanks will generally be around 0.5 – 1.0 % dry solids content
Sludge management (e.g. pressing or sludge storage)	VOCs as fugitive emissions. Gases from solution		
Solvent extraction	Solvents as fugitive emissions. Significant potential for emissions on transfer and emergency releases	Solvents	
Stripping	Emissions are trapped in the areas provided in the Ph-c plant		

**Table 3.23: Emissions from physico-chemical treatment processes applied to waste water**

[55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [121, Schmidt and Institute for environmental and waste management, 2002]

### 3.3.2. Emissions from the physico-chemical treatment of waste solids and sludges

The emissions listed in Table 3.24 below can be expected to occur from most treatment plants. The scale of the emission depends on the plant throughput and on the abatement systems applied.

Physico-chemical activity	Air	Water	Residues/Soil
Filtration/pressing	Ammonia and, if there is a high organic content in the wastestreams, VOCs		
Buildings for immobilisation mixing	Emissions via roof vents. Emissions occur during transfer from the mixing pit to removal off-site; and via access doors from spillages/leaks during charging of the reaction vessels		
Sludge blending	Particulate matter and VOCs, particularly if an exothermic reaction occurs		
Sludge management (e.g. pressing or sludge storage)	VOCs as fugitive emissions. Gases from solutions		
Solidification	There is a potential for particulate emissions from this operation		
Automated charging of waste	VOC, dust odour during the transfer of wastes and reagent		
Reaction vessel	Emission occur due to the reaction of incompatible substances. Uncontrollable reactions due to incorrect dosing of reactants or the formation of hot spots through poor mixing	Leakage through badly maintained or damaged equipment	Leakage through badly maintained or damaged equipment
Reagent silo	Dust arises from the overfilling of reagent silos. Also fugitive dust emissions from silo connections and dust from reagent stockpiles stored loose		

**Table 3.24: Emissions from physico-chemical treatment processes applied to solids and sludges**  
[55, UK EA, 2001], [56, Babbie Group Ltd, 2002]

The fugitive emissions from material handling operations for *ex situ* processes are often overlooked or ignored, but they may represent a significant fraction of the total emissions from the soil treatment.

#### Emissions from soil excavation and removal activities

VOC emissions from handling operations in soil excavation and removal result from the exchange of contaminant-laden soil-pore gas with the atmosphere when soil is disturbed, and from some diffusion of the

contaminants through the soil. There are several potential emission points involved in excavation; all are considered to be fugitive area sources. For excavation, the main emission points of concern are emissions from:

- exposed waste in the excavation pit
- material as it is dumped from the excavation bucket, and
- waste/soil in short-term storage piles.

In addition, the earth-moving equipment will involve additional sources of emissions of VOC, particulate matter, nitrogen oxides, etc. It is known that large amounts of VOCs may be released from soil during handling, so VOCs are typically the emissions of most concern. Emissions of particulate matter and associated metals and semi-volatile compounds may be of concern at particular sites.

Given the frequency with which the excavation of contaminated soils is carried out, surprisingly little air emission or emission rate data for excavation have been published.

However, some measured emission rates for two sites for combined excavation and dumping operations are available and quote figures as high as 4 g/min for specific compounds. Here, most of the VOCs present in the soil was stripped from the soil during excavation, based on a comparison of measured total emissions versus the mass of these same contaminants in the soil (calculated from soil concentration data). This was true for both sites, despite differences in soil concentrations and soil type.

Activity	Sludge volume (m <sup>3</sup> )	Exposed surface area (m <sup>2</sup> )	C <sub>8+</sub> hydrocarbon emission rate (g/s)	C <sub>8+</sub> emission flux (g/m <sup>2</sup> /s)
Sludge disturbance	25 – 27	45 – 125	1.33	0.01 – 0.03
Sludge excavation	26 – 48	125 – 261	7.76	0.03 – 0.06
Sludge dewatering	1.7	3.3	1.24	0.38
Post-disturbance	26	91	1.11	0.01

**Table 3.25: Results of emission measurements**  
Based on [30, Eklund, et al., 1997]

The magnitude of volatile organic compound (VOC) emissions depends on a number of factors, including the type of compounds present in the waste, the concentration and distribution of the compounds, and the porosity and moisture content of the soil. The key operational parameters are the duration and liveliness of the handling, and the size of equipment used. The longer or more energetic the moving and handling, the greater likelihood that organic compounds will be volatilised. The larger the volumes of material being handled per unit operation, the lower the percentage of VOCs that are stripped from the soil, because the surface area to volume ratio is minimised.

Soil containing benzene or other volatile carcinogens would likely pose a large risk to on-site workers and the surrounding populace if it were to be excavated.

The magnitude of emissions from soil handling operations will vary with the operating conditions. The rate of excavation and dumping, the drop height, the amount of exposed surface area, the length of time that the soil is exposed, the shape of the storage piles, and the dryness of the surface soil layers will all influence the levels of VOC emissions. Add-on control technologies are available for minimising emissions, but these are relatively ineffective and costly to implement compared with the controls for point sources.

#### **Emissions from thermal desorption**

Air emissions from thermal desorption systems are influenced by the waste characteristics, the desorption process applied, and the emissions control equipment used. The air emissions associated with thermal desorption come from several sources. The point sources of air emissions vary widely with each process. The stack of an afterburner vents combustion products, as does a fuel-fired heating system if the combustion gases are not fed into the desorber. A fuel-fired heating system typically operates with propane, natural gas, or fuel oil. If the VOC emission controls consist of a baghouse, scrubber, and vapour phase carbon adsorber, the off-



gas will contain small concentrations of the original contaminants, as well as the products of any chemical reactions that might occur. The volume of off-gas from a thermal desorption unit depends on the type of processor. Table 3.26 below gives some values for emissions from thermal desorption.

	Flow of gases (Nm <sup>3</sup> /h)	Pollutants that may be contained
Direct heating	17000 – 85000	VOC
Indirect heating	1700 – 8500	VOC

**Table 3.26: Emissions from direct and indirect heating thermal desorption**  
[30, Eklund, et al., 1997]

Various types of thermal desorption systems can produce up to nine residual process streams: treated soil, oversized media rejects, condensed contaminants, water, particulate control dust, clean off-gas, phase separator sludge, aqueous-phase spent carbon, and vapour- phase spent carbon. Off-gases from indirectly heated units, i.e. thermal screws, can be treated with smaller chemical/physical systems, such as a baghouse or a condenser, followed by an afterburner.

Pollutant	From
Fugitive emissions	<ul style="list-style-type: none"> <li>excavation of contaminated soil</li> <li>classifier, feed conveyor, and the feed hopper</li> <li>components of the thermal desorption system and controls</li> <li>exhaust gases from the heating system, treated soil, particulate control dust, untreated oil from the oil/water separator, spent carbon from liquid or vapour phase carbon adsorber, treated water, and scrubber sludge</li> </ul>
Particulate matter, nitrogen oxides (NO <sub>x</sub> ), carbon monoxide (CO) and acid gases	Combustion and pyrolysis
Dioxins, furans and phenol	

**Table 3.27: Generic emissions from thermal desorption**  
[30, Eklund, et al., 1997]

Parameter	Initial concentration <sup>1</sup> (ppm)	Final concentration <sup>1</sup> (ppm)	Removal efficiency (%)	Typical off-gas characteristics <sup>2</sup> stack concentration
PM		700 – 1000 mg/Nm <sup>3</sup>		
Benzene	0.11 – 39.5	<0.01 – 0.06	84.5 – 99.9	4.3 – 8.6 ppm
Toluene	0.27 – 2	<0.01 – 0.1	n/a	0.6 – 0.8 ppm
m,p-Xylenes	<0.8 – 3	0.2 – 1.2	<75	0.42 – 3.5 ppm
o-Xylenes	3.1 – 15.6	<0.01	99.7 – 99.9	
Total Xylenes	13.1	0.1	99.2	
Ethylbenzene	0.11	<0.01	>90	
THC	39 – 393	5.7 – 9.5	85 – 97.5	129 – 2800 ppm
VOC		0.045 – 2.27 kg/h		
Diesel	1875	<1	>99.9	
Naphthalene				5136 – 6757 µg/Nm <sup>3</sup>
Acenaphthylene				634 – 901 µg/Nm <sup>3</sup>
Acenaphthene				317 – 638 µg/Nm <sup>3</sup>
Fluoranthene				405 – 763 µg/Nm <sup>3</sup>
Phenanthrene				385 – 645 µg/Nm <sup>3</sup>
Anthracene				<1.4 – 427 µg/Nm <sup>3</sup>
Fluoranthene				24 – 135 µg/Nm <sup>3</sup>
Pyrene				32 – 111 µg/Nm <sup>3</sup>

<sup>1</sup> Based on two or three installations depending on the parameter.

<sup>2</sup> Based on two installations. Emission control equipment consists of a wet scrubber and cyclonic demister. ppm values referred to dry conditions

The VOC emissions from asphalt aggregate dryers will vary by several orders of magnitude depending on whether afterburners are used as a control device. These treatment systems typically do not employ VOC controls, unless they have been modified for soil remediation.

A company has estimated the typical emissions for soil treatment in a modified asphalt aggregate dryer. This system consists of a direct-fired rotary drum operating at 290 – 540 °C. A primary cyclonic tube collector and pulse-jet baghouse are used to control particulate emissions. A thermal oxidiser (i.e. an afterburner) destroys organic compounds in the off-gas stream (99 – 99.99 % efficiency). Based on a processing rate of 32 – 54 t/h.

**Table 3.28: Characteristics of inputs and outputs of asphalt aggregate dryers**  
[30, Eklund, et al., 1997]

Contaminant	Units	Residence time (minutes)	Temperature (°C)	Initial concentration	Final concentration	Rate of uncontrolled emissions (g/h)	Estimated emissions rate (g/h)
PCBs	ppm	19	550	37.5	2	1.14	5.68e-02
2,3,7,8-TCDD	ppb	40	560	260	0.018	0.00832	4.16e-04
	ppb	19	560	236	0.018	0.00755	3.78e-04
	ppb	10.5	560	266	0.018	0.00851	4.26e-04
	ppb	24	460	233	0.5	0.00744	3.72e-04
	ppb	5.6	550	48	0.084	0.00153	7.67e-05
	ppb	20	555	56	0.23	0.00178	8.92e-05

Overall estimated efficiency is 95 %

**Table 3.29: Estimated emissions of selected compounds for the clean-up of PCB contaminated soil using a thermal desorption process**  
[30, Eklund, et al., 1997]

#### Emissions from vapour extraction of solid waste

The air emissions associated with vapour extraction systems come primarily from the stack. Additional releases of volatile organics may occur from the treatment of any contaminated water that is extracted. Fugitive emissions are considered negligible due to the negative pressure throughout most of the system.

Emissions include untreated volatile organics from the extraction process. A removal and subsequent emission of semi-volatile organic compounds will also occur, though less efficiently than for VOCs. There may also be smaller amounts of air emissions associated with the control system. Due to the variety of technologies used for vapour treatment, stack emissions may also include some products of incomplete combustion, NO<sub>x</sub>, particulate matter, CO, and acid gases. Of primary concern, however, are the volatile organics emitted from the point sources. Air emission data for several vapour extraction systems are summarised in Table 3.30.

No. of systems surveyed	Parameter	Units	Range or value	Approximate average
13	Flowrate per well	m <sup>3</sup> /min	0.2 – 8	2
	Removal	kg/day	0.9 – 113	27
	Exhaust gas concentration	ppmv	20 – 350	100
17	Total flowrate	m <sup>3</sup> /min	0.1 – 161	23
	Treatment:	n° systems		
	• none		9	
	• carbon		6	
	• catalytic incineration		1	
	• combustion		1	
17	Removal rate	kg/day	2 – 195	45
	Total flowrate	m <sup>3</sup> /min	0.7 – 318	62
	Pollutant concentration	ppmv	150 – 3000	400
	Control efficiency	%	90 – 99	95

**Table 3.30: Emissions from vapour extraction systems**  
[30, Eklund, et al., 1997]

The emission rate of VOC compounds over time from continuously operated vapour extraction systems tends to show an exponential-type decay curve.

Pollutant	Peak uncontrolled stack emissions <sup>1</sup> (g/h)	Peak controlled stack emissions <sup>2</sup> (g/h)
Trichloroethylene (TCE)	1712	17.1
trans-1,2-Dichloroethylene (DCE)	99.4	0.99
1,1,1-Trichloroethane (TCA)	13.6	0.14
Tetrachloroethylene (PCE)	3.18	0.03
<b>TOTALS</b>	<b>1830</b>	<b>18.3</b>
<sup>1</sup> Uncontrolled emissions based on the removal rate of each contaminant		
<sup>2</sup> Based on estimated 99 % overall control efficiency for two carbon adsorption canisters in series		

**Table 3.31: Estimated emissions for an in-situ vacuum extraction system**  
[30, Eklund, et al., 1997]

#### Emissions from soil washing

In the soil washing process, the greatest potential for emissions of volatile contaminants occurs in the excavation, materials handling, feed preparation, and extraction processes. The waste streams also have the potential to be sources of VOC emissions. The solvent recovery process involves vaporisation of the solvent, so fugitive emissions are possible from this as well as from other stages of the solvent process. Waste streams also have the potential to be sources of VOC emissions if any VOCs are already present in the waste stream. For solvent extraction processes, emissions of the solvent itself also may be a cause for concern.

Storage areas need to be kept under specific control to avoid pollution dispersion, especially of dust. For liquid effluents, the plants are always equipped with a water-slurry treatment unit, where the water is sent before being discharged.

Soil washing generates four waste streams: contaminated solids separated from the wash-water; waste water; waste water treatment sludge and residual solids; and air emissions.

208. Water parameter	209. Concentration (mg/l)
210. Suspended solids	211.60
212. BOD <sub>5</sub>	213.25
214. COD	215.350
216. Nitrit N (NO <sub>2</sub> -N)	217.10
218. P, total	219.2
220. Cr, total	221.0.3
222. Cu	223.0.5
224. Hg	225.0.005
226. Ni	227.0.3
228. Pb	229.0.3
230. Zn	231.2
232. Residues generated by the process <sup>1</sup>	233.
234. Sludges	235. Mineral sludges
236. Other residual fractions	237. Particle PAHs and metal oxides
238. <sup>1</sup> The subsequent fate of these residues are reported to be landfill	

**Table 3.32: Emissions from an installation treating contaminated soil by washing [66, TWG, 2003]**

**Note: Capacity of the installation is 68 kt/yr**

#### Emissions from solvent extraction

Up to five waste streams may result from the solvent extraction process: concentrated contaminants; solids; waste water; oversized rejects; and treated air emissions.

Solvent extraction units will be of a closed-loop design in which the solvent is recycled and re-used. Typically, solvent extraction units are designed to produce negligible air emissions, but some solvents have been detected in the off-gas vent system. In addition, significant levels of emissions (both vapour-phase and particulate matter) may occur during waste preparation activities such as excavation and materials handling.

#### Emission from treatments of FGT waste

The main environmental concern related to handling, utilisation and disposal of combustion wastes is the potential emission of heavy metals, organic pollutants and salts. The main pathways for this are by leaching and by airborne dust emission. As airborne emissions can be controlled relatively easy, leaching is an environmentally more important issue. It should also be noted that hydrogen gas generation from FGT waste by contact with water has been documented and can potentially cause considerable problems. Its generation is dependent on intermediate FGT waste storage and the type, design and operation of the landfill that it may be developed.

#### Emissions from stabilisation methods

Several of the stabilisation methods have an initial washing step, where a major part of soluble salts and, to some extent, metals are extracted before chemical binding of the remaining metals. These methods are finalised by dewatering the stabilised product, which will then be ready for landfilling. Then, washing solid waste generates a waste water that needs some sort of treatment because of the content of some components. However, depending on the local authorities, such generated waste water may be discharged into the environment or treated in the chemical industry to recover some salts (e.g. sodium salts).

### Emission from asbestos treatments

The fibrous nature and the size of the fibres are the main parameters that makes asbestos dangerous. During treatment some emissions may be generated.

### 3.3.3. Emissions from the treatment of specific wastes

#### Hydrogenation of POPs

At a Canadian facility, product gas was found to contain no detectable PCBs, while concentrations of total chlorobenzenes and dioxins were similar to those of the blanks. This suggests that the product gas did not contain quantifiable levels of these substances. When the product gas was burned in the steam reformer, dioxins were emitted from the reformer stack at a concentration of 15 pg TEQ/Nm<sup>3</sup>. This dioxin formation was attributed to the use of PCB contaminated air from the site of the reformer's combustion air.

All outputs from the destruction of PCB contaminated waste using this process can be contained and tested. There are no uncontrolled emissions from the process which could result in releases of PCB contaminated air, solids, or liquids to the surrounding environment. Releases of PCBs to the environment could only occur during waste handling prior to treatment, where the possibility of spillage exists.

Because the reaction takes place in a reducing atmosphere in the absence of oxygen, the possibility of dioxin and furan formation is said to be eliminated. If the hydrogen (dry basis) content is maintained at percentages greater than 50 %, the formation of PAHs is prevented.

Type of waste	Destruction efficiency (%)	DRE (%)
PCB oils	99.999808 – 99.9999996	99.9999985 – 99.9999997
chlorobenzenes	99.9999836 – 99.9999972	99.9999842 – 99.9999985
Dioxins present in PCB oils	99.999 – 99.9999	

**Table 3.33: Reported destruction efficiency of hydrogenation processes**  
[100, UNEP, 2000]

If either the product gas or the ambient air used as combustion air for the boiler or similar units contains hydrogen chloride or other chlorinated species, dioxins may be generated during their combustion. In order to meet the fundamental technical criteria for POPs destruction, both the product gas and combustion air must be treated to remove such chlorine donors and so prevent dioxin formation.

Care is required to avoid high rates of gas generation, which could over-pressurise systems. The process has a limited surge capacity: over-pressurisation could therefore result in the release of waste material.

During typical operations, 30 to 50 % of the product gas is burned as fuel for the boiler or other auxiliary units.

Residues generated by the process include product gas from the reactor, scrubber water and sludge from product gas treatment, and small quantities of grit from the reactor. The product gas is either catalytically reformed to recover hydrogen or burned as fuel in one or more of the auxiliary systems – the boiler, catalytic reformer and/or sequencing batch vaporiser.

#### Hydrogenation of PCBs and POPs

All emissions and residues are captured for assay and reprocessing, if needed. Destruction rates ranging from 99.9 to 99.99999 % have been reported at sites operating on a commercial scale in Australia.

#### Supercritical water oxidation

Process residues are usually contained and consist of water, gas (less than 10 ppm of CO and very low amounts of oxides of nitrogen, acid gases such as hydrogen chloride or sulphur oxides and particulates) and solids if the waste contains inorganic salts or organics with halogens, sulphur or phosphorus. Residues generated during the process such as ash and brine require disposal.

### 3.4. Waste OUT from physico-chemical treatments

Much of the waste OUT from these processes goes to landfilling.

#### Waste waters

The essential mass flow from Ph-c plants is the waste water, corresponding to about 85 to 95 % of the mass of the waste accepted for treatment. The waste water quality of Ph-c plants is regularly monitored by the supervisory authorities and within a framework of self-monitoring. Due to this monitoring activity, extensive data are available on the composition of waste water from Ph-c plants.

Water emission parameters	Ranges values of the annual average values (ppm)	Ranges of annual charge (kg/yr)
pH	6.9 – 10.4	
Electric conductivity	1150 – 13500 $\mu$ S/cm	
Transparency (view depth)	10 – 47 cm	
Suspended solids	<0.5 – 32 <0.1 – 2.1 ml/l	<0.6
TOC	2200 – 3800	38061
BOD	5 – 2490	
COD <sup>1</sup>	200 – 17870	
Hydrocarbons	<0.1 – 19.8	89
Detergents (anionics)	0.6 – 14.8	
Mineral oil	5 – 10	
Phenol index	0.8 – 25	317
AOX	<0.01 – 0.7	9
EOX	<0.1 – 0.5	
BTX	<0.1 – 1.2	10
Cl	3975 – 35420	
Cl free	<0.1 – 0.3	
CN	<0.1 – 0.6	<1
CN free	<0.01 – 0.1	
F	0.5 – 8.6	
N - organic	109 – 440	
N - total	8.4 – 590	
NH <sub>3</sub> -N	22 – 1330	
Nitrate-N	0.9 – 472	
Nitrite-N	0.90 – 10.2	38
P - total	<0.1 – 14.75	
Sulphate	65 – 3630	
Sulphide	1012	
Sulphide free	<0.1 – 0.77	<1
Al	<0.1 – 5	63
As	<0.01 – 0.1	<0.1
Cd	0.0004 – 0.1	
Co	≤ 0.1	
Cr total	0.05 – 0.3	3.8
Cr (VI)	<0.01 – 0.1	<1
Cu	<0.1 – 0.4	2.5
Fe	0.2 – 20	253
Hg	0.0001 – 0.02	<0.02
Mn	<0.1 – 2.7	
Ni	0.05 – 1.4	3.8

Pb	<0.02 – 0.7	<1
Se	<0.1 – 0.5	
Sn	<0.1 – 0.4	
Zn	<0.1 – 3.9	12
Notes: Ranges have been constructed from several sets of emission data provided. A data set is based on the data from Ph-c plant operators with a total capacity of 850 kt/yr. The data correspond to year 2001. The average age of the plants is about 17 years (ranging from 4 to 39 years). Approximately 84 % (from 73 to 91 %) of all the Ph-c plants for the treatment of accepted waste covered here, can be attributed to EWL groups 11,12,13,16 and 19. Another set corresponds to 20/80 percentile of the annual average values for some Ph-c plants, and another to measured minimum/maximum values found in demulsification plant treatment (data from 1994 – 1999)		
<sup>1</sup> Some data relate to THE dissolved COD fraction and other correspond to the total COD		

**Table 3.34: Waste OUT from the physico-chemical treatment of contaminated waters**  
[121, Schmidt and Institute for environmental and waste management, 2002], [134, UBA, 2003], [150, TWG, 2004], [156, VROM, 2004], [157, UBA, 2004]

Outputs of lacquer treatment facility are shown in Table 3.35 below:

Material	Amount (t/yr)	Composition (mg/kg)
Dried material	10000	PCB <0.05
		BTEX 104.8
		As <1
		Cd 6.7
		Cr total 77
		Cu 905
		Hg 0.25
		Ni 43
		Pb 339
		Tl <0.5
		Cyanide total 6200
Organic process water	2000	Cd <0.5
		Hg <0.5
		Zn 1.7
Solvent reclaim	13000	

**Table 3.35: Waste OUT of physico-chemical treatment of contaminated water treating mainly lacquer coagulum and solvents**  
[135, UBA, 2003]

Table 3.36 shows the emission levels achieved after a polishing step of the effluent, e.g. by sand filtration or ion exchange filters.

Compound	Concentration (mg/l waste water) (24 hour samples)
Free cyanide	1.0/0.2
Halogenated VOCs	0.1
Mineral oil	200 (random sample)
Ag	1.0/0.1
Cd	0.2
Cr (total)	1.0/0.5 <sup>1</sup>
Cr(VI)	0.1
Cu	2.0/0.5
Ni	2.0/0.5

Pb	2.0/0.5
Sn	3.0/2.0
Zn	2.0/0.5
<sup>1</sup> standards for discharged load of metals (Cr, Cu, Ni, Pb and Zn) <200 g/day and >200 g/day	

**Table 3.36: Emission levels achieved after a polishing step of the effluent, e.g. by sand filtration or ion exchange filters**  
[156, VROM, 2004]

#### Waste solids and sludges

The final material after stabilisation/solidification will have a similar composition of metals and organic content as the original waste. However, the final material has a reduced toxicity and solubility of metals and organic compounds compared to the original waste.

The annex of the Landfill Directive (EC 33/2003) contains the criteria and procedures for the acceptance of waste at landfills. The criteria contain some limit values for hazardous waste acceptable at different types of landfills. These are based on leaching limit values and restrict some metals, some anions and organic compound parameters.

Water permeability of stabilised waste depends on many parameters (e.g. nature of the waste, nature and amount of added reagent, aimed objectives) so permeability values may vary from  $10^{-9}$  to  $10^{-12}$  m/s.

#### Immobilised bottom ash/slag

In general, there are several possibilities employed for the re-use of bottom ash, after treatment. When the slag values do not meet defined parameters, a slag re-use with defined technical safety measures is possible. Some examples of re-use options are described below and are shown in Table 3.37:

- used in road and street construction. The bottom ash is used as a solid base for at the construction of, e.g. parking places, airports and harbour areas. However, there is a need for an impermeable layer which coaches over the bottom ash layer to avoid leaching, this can be asphalt or perhaps concrete
- used in soil constructions, e.g. road embankments or noise protection walls. It is important that the area where bottom ash will be used has to be a hydrogeologically favourable land. This means that there has to be a layer of 2 meters of clay or loam which protects the groundwater from adverse effects. Furthermore, there has to be a mineral surface which is impermeable ( $d > 0.5$  m and  $k_f < 10^{-8}$  m/s)
- used in important water management zones and in hydrogeologically sensitive areas and is subject to exception for individual case inspections.

239. Recycling paths of treated bottom ash/slag	240. %
241. Anti-freeze course	242.27
243. Filling material	244.22
245. Ballast substructure	246.11
247. Improvement of land	248.9
249. Base frame/dam construction	250.5
251. Land consolidation	252.5
253. Noise protection wal	254.3
255. Landscaping	256.1
257. Unbound street and road construction	258.1
259. Others	260.16

**Table 3.37: Recycling paths of the mineral fraction of treated bottom ash in Germany**  
[150, TWG, 2004]

The following Table 3.38 and Table 3.39 below characterise the important bottom ash parameters after a physico-chemical treatment process.



261.Metals	262.Minimum	263.Average	264.Maximum
265.As	266.0	267. 0.074 – 0.15	268.0.187
269.Cd	270.0.0008	271. 0.0037 – 0.01	272.0.0167
273.Cr	274.0.067	275. 0.172 – 0.6	276.0.726
277.Cu	278.0.150	279. 0.6 – 6.826	280.29.781
281.Hg	282.0	283. 0.01 – 0.07	284.0.37
285.Ni	286.0.023	287. 0.165 – 0.6	288.0.661
289.Pb	290.0.19	291. 1 – 1.222	292.4.063
293.Tl	294.0	295.	296.
297.Zn	298.0.470	299. 1.5 – 2.970	300.14.356
301. Units: in g/kg, except Hg that is in mg/kg			
302. Zero in this table means below analysis detection limit			

**Table 3.38: Metal composition of treated bottom ash after treatment (solid analyses)**  
[89, Germany, 2003], [150, TWG, 2004]

303.Chemicals	304.Minimum	305.Average	306.Maximum
307.Cl	308. 29	309.	310.
311.Sulphates	312. 43	313.	314.
315.CN total	316. 0	317.	318.
319.Phenol index	320. 0	321.	322.
323.As	324.1.3	325. 5.3	326.16.1
327.Cd	328.0	329. 0.8	330.5
331.Cr	332.0	333. 15.2	334.200
335.Cu	336.0	337. 60.7	338.300
339.Hg	340.0	341. <0.2	342.1
343.Ni	344.0	345. 2.9	346.40
347.Pb	348.0	349. 11.4	350.59.0
351.Tl	352.2	353.	354.
355.Zn	356.0	357. 19.4	358.300
359. Units in µg/l			
360.Zero in this table means below analysis detection limit			

**Table 3.39: Eluate analysis of bottom ash quality after treatment**  
[89, Germany, 2003], [150, TWG, 2004]

#### Waste OUT from a classical soil washing unit

Generally, soil washing units produce recycled materials suitable for the construction industry (concrete producers, asphalt plants) or as refilling materials after internal quality control and external control have been carried out on the specific properties of the materials (to ensure compliance with local regulations)

Different fractions can be distinguished:

- coarse fraction: gravels which can be calibrated in several ways. These are basically formed by fine gravels measuring 2 – 20 mm and coarse gravels measuring 20 – 80 mm
- sand fraction: consist of sand generally sized from 60 µm to 2 mm
- residual organic fraction (>60 µm): these fractions are incinerated or sent to an appropriate landfill
- fine residual fraction (filter cake <60 µm): usually this is sent to a special landfill with or without additional treatment (e.g. inertisation, stabilisation) or may be sent for a further treatment if required (e.g. thermal desorption, classical incineration).

361.	362.Capacity (t/yr)
363.Waste IN	364.68000
365.Waste OUT	366.50500
• sand	367.36000
• gravel	368.13000
• fines	369.1500

**Table 3.40: Waste OUT of a installation treating contaminated soil by washing**  
[66, TWG, 2003]

#### Waste OUT from excavation

Excavation has been found to decrease the soil moisture content and the dry bulk density of the soil. Data show that the water content fraction decreases by 35 % to 56 % and the dry bulk density of the soil decrease by 13 %.

#### Waste OUT from thermal distillative drying

The dry residue of the treatment of aerosol cans is separated into steel and waste aluminium before smelting. These metal fractions fulfil all acceptance criteria of the steel mill operations. The condensates from the drying process consist of complex solvent mixtures that may only be used thermally or have to be incinerated. When unused faulty aerosol cans are treated, it may be discussed in advance with the producer if recycling of the contained solvents is also possible.

#### Waste OUT from a CFC treatment plant

Table 3.41 below shows the specification of the products achieved by the cracking of the CFC solvents.

Parameters	Unit	Target	Actual value
Water content	ppm	<50	34
Oil content	ppm	<100	60
Amine content	ppm	<100	10
Acid	ppm	<1	0.03
Halogens	vol-%	<0.1	0.004
PCB and PCT	vol-%	0	0
Information from a CFC distillation plant of Figure 2.5 shown in Section 2.5 This interconnection treatment facility converts CFCs into hydrochloric acid and hydrofluoric acid.			

**Table 3.41: Specification of CFC cracked products**

[147, UBA, 2003], [150, TWG, 2004]

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## 3.5. Monitoring

### Monitoring practices in physico-chemical treatment plants of waste waters

The monitoring issues with the physico-chemical treatment of waste waters cover:

- wastes containing phosphorus: not all sites are required to monitor regularly for total phosphorus so it may be easier to make an estimate of this emission from the intake of phosphoric acid
- occasional inorganic wastes: for example wastes containing arsenic. Again, it is easier to calculate the annual emission from occasional waste IN data than to extend the monitoring programme.

Emissions to the air are the least well monitored discharges from physico-chemical treatment plants.

The main discharges to the air could be based on monitoring, but fugitive emissions will need to be estimated, as will the possibility of organic contaminants.

Almost all Ph-c sites have a complex set of conditions relating to water discharge that regulate sampling and monitoring frequency, and which set both the maximum concentration allowed for different species in the effluent and a maximum daily, weekly or monthly quantity of different species. This requires flow proportional monitoring, or the monitoring of each batch before discharge of a set volume. Either system provides the data to calculate annual emissions for a number of main species. The problem in estimating emissions to water is restricted to those species that are known to exist, but for which there is no monitoring data, and to unexpected species that arrive with particular waste streams. Other inorganic species, such as arsenic, could probably be estimated from site intake data since treatments of wastes contaminated with those components are typically occasional activities.

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## 4. Techniques to consider in the determination of BAT

### Techniques for physico-chemical treatments

This section contains techniques considered to have a good environmental operating performance (e.g. use of a good energy system) or that can help lead to a good environmental performance (e.g. environmental management systems). Techniques in this section relate to physico-chemical treatments described in Section 2.3.

#### 4.1. Techniques used in physico-chemical treatment plants of waste waters

##### 4.1.1. Planning the operation of a Ph-c plant

###### Description

The following principles have to be followed:

- a. all measurement and control installations have to be easily accessible and easy to maintain
- b. control and testing system have to be established
- c. the reception inspection need to be adapted to the information from the declaration analysis of the proof of waste disposal and to the process order provided for each particular treatment
- d. the production of waste water should be prevented as far as possible by construction measures, e.g. roofing of the reception area
- e. in order to prevent unwanted mixing, the reaction containers should also serve as storage containers
- f. adequate storage capacity has to be provided, since the time of demand and delivery usually do not coincide
- g. the plant concept should provide for potential modification or expansion
- h. collection and transport of wastes as well as delivery (quantity, time) should be adjusted to the operation
- i. producers and distributors should be addressed for all technical details and information (e.g. about containers, pipes, pumps, valves and filters),
- j. planning and construction (especially legal matters) should be discussed early with the responsible authorities and with technical planning offices.

###### Achieved environmental benefits

Emissions are reduced as the correct treatment procedure is established in the Ph-c plant.

###### Operational data

The design of a Ph-c plant is set in a clear way which follows the material flow. For example, two fundamentally different cases need to be distinguished:

1. dimensioning of a plant which treats similar waste types
2. dimensioning of a plant which treats varying waste types.

In case (1), the plant can be developed by means of experiments that are specifically tailored to the waste requirements. The necessary process steps can be tested individually or in combination; the result is an optimal treatment solution. In case (2), different treatment processes have to be planned that lead to optimal treatment when applied in combination. In addition, while in case (1) continuously operated plants seem appropriate, in case (2), discontinuous operation should be recommended because of adjustment of the technology and operation mode to different reactive behaviour of the wastes.

###### Applicability

Applicable to new installations.

#### 4.1.2. Techniques for Ph-c reactors

##### Description

Some techniques include:

- a. clearly defining, the objectives and the expected reaction chemistry for each treatment process. There needs to be a defined end-point to the process so that the reaction can be monitored and controlled. The suitable inputs to the process need to be defined and the design needs to take into account the likely variables expected within the waste stream
- b. assessing each new set of reactions and proposed mixes of wastes and reagents prior to treatment in a laboratory scale test mix of the wastes and reagents to be used. This needs to lead to all reactions that will occur in the full scale treatment and so the mixing of wastes needs to be done to a pre-determined batch 'recipe'. This needs to take into account the potential scale-up effects, for example, the increased heat of reaction with the increased reaction mass relative to the reactor volume, increased residence time within the reactor and modified reaction properties, etc.
- c. specifically designing and operating the reactor vessel so that it is fit for its intended purpose. Such designs need to include considerations of the chemical process hazards, a hazard assessment of the chemical reactions, considerations of appropriate prevention and protection measures, together with consideration of the planned process management, that is, working instructions, staff training, plant maintenance, checks, audits and emergency procedures
- d. enclosing all treatment/reaction vessels and ensuring that they are vented to the air via an appropriate scrubbing and abatement system
- e. where appropriate, ensuring that the reactor vessels (or the mixing vessels where the treatment is carried out) are charged with premixed wastes and reagents. For example some reactor vessels may need to be 'pre-limed' or charged first with the reacting alkali to control the reaction, using for example calcium hydroxide solution made up prior to charging the reactor vessel
- f. avoiding decanting the sacks or drums directly to the vessel. This practice can lead to:
  - concentration 'hotspots' at the surface of the reaction liquor
  - a loss of reaction control
  - the emission of fumes from the instantaneous reaction at the interface
  - the open hatch venting fumes and thus bypassing the appropriate abatement
- g. monitoring the reaction to ensure that it is under control and proceeding towards the anticipated result. For this purpose, the vessels used for treatment need to be equipped with high level pH and temperature monitors. These need to be automatic and continuous and linked to a clear display in the control room or laboratory, together with an audible alarm. A risk assessment may require process monitors to be linked to cut-off devices. Monitoring of the reaction is necessary because the reaction characteristics in the reactor may vary from those found in the laboratory tests. Monitoring needs to provide an early indication of any deviation from the laboratory tests, and also needs to enable measures to be taken to halt or modify the reaction. There should, consequently, be a provision for the cooling and/or quenching of reactor vessels
- h. ensuring that there is adequate mixing within a treatment vessel as this may determine the success of the reactor. The standard method for agitating the contents of a vessel is a rotating impeller. There is a geometric ratio between the size of the impeller and the clearance from the vessel (determined by type and size of vessel). This also depends on the agitation speed and characteristics of the waste. A seal is required where the impeller enters the vessel to prevent fugitive releases. A method of mixing should be provided
- i. in order to track and control the process of change, keeping a written procedure for the proposal, consideration and approval of any changes or technical developments including all procedural or quality changes
- j. ensuring that any VOCs that are emitted due to the high temperature rise in the reaction vessels are returned to the treatment system after condensation in the scrubbers
- k. monitoring the reaction throughout the course of the reaction. It may be necessary to extract the exhaust air of the reactor

- 
- l. having a system, as is the case at most sites, to exchange the air above the reaction vessels and to pass it through some type of treatment system to remove gases such as ammonia, hydrogen chloride, sulphur dioxide. Typically aqueous liquors from scrubbers are returned to the treatment plant, and activated carbon systems are regenerated (e.g. by steam stripping) or in case this is not possible, the activated carbon is incinerated.

#### **Achieved environmental benefits**

Control of the reaction/treatment process is crucial to environmental protection and to preventing possible accidents. A yield of 96 % removal of metals can be attained.

#### **Applicability**

Physico-chemical plants undertake input waste screening to enable them to store wastes in the correct tanks and to balance the reactions.

#### **Driving force for implementation**

Some national effluent standards are available, e.g. the Surface Waters Pollution Act in the Netherlands.

#### **Example plants**

In general, neutralisation reaction tanks are fitted with alkaline scrubber units and most of the acid gases are returned to the process along with some of the VOCs and almost all of particulate matter/liquors. The capacities of the example plants vary from 200 to 40000 m<sup>3</sup>/yr.

#### **Reference literature**

[55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004], [156, VROM, 2004]

### **4.1.3. Neutralisation**

#### **Description**

The purpose and principle of operation of the neutralisation is shown in Section 2.2. Some issues to consider include:

- preventing the mixing of acidic/basic waste with other streams to be neutralised when the mix contains metals and complexing agents at the same time. This prevents the formation of metal complexes that are difficult (from an economic point of view) to separate afterwards. Complexing ions to watch out for include, for example, EDTA, NTA and cyanides
- making the necessary neutralisation equipment robust and easy to use can help the equipment stand up to the vigours of use in Ph-c plants dealing with acidic/basic wastes needing neutralisation
- ensuring that the customary measurement methods, i.e. with the aid of glass electrodes or similar sensors, are used in Ph-c plant operation for the neutralisation of waste matter if the electrodes are constantly cleaned and properly calibrated. Determination of the pH value is also possible by the measurement of prepared samples or by measurement using litmus paper
- separately storing the neutralised waste water in order to avoid negatively affecting the quality of the treated waste water due to secondary reactions occurring if they were stored together. Final inspection of the treated waste water needs to be performed after a sufficient storage time has elapsed.

#### **Achieved environmental benefits**

Improves the neutralisation process performance and avoids downstream problems (e.g. preventing the mixing of wastes or other streams in a way that further treatment of the waste water is no longer possible).

#### **Operational data**

If sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and milk of lime (Ca(OH)<sub>2</sub>) are combined, gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) may be produced as a reaction product. The gypsum may lead to deposits and incrustation, causing serious operational disruption and necessitating extensive maintenance and repair measures. However, these problems can be minimised by adequate operation of the neutralisation process (using diluted H<sub>2</sub>SO<sub>4</sub> and pre-neutralisation with lime) and

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vigorous mixing. If NaOH instead of lime is used for neutralisation, other problems may occur. According to some experiences, high sulphate concentrations in the waste water caused by NaOH neutralisation may attack sewers made of concrete and consequently lead to odour emissions.

#### **Applicability**

Neutralisation can be applied with all mixable liquid waste.

#### **Example plants**

In a dilute aqueous system, it should be possible to conduct neutralisation processes without either deliberately or inadvertently producing gases. In such system processes involving potentially hazardous substances, for example, acid neutralisation can normally be performed without creating substances that require continuous abatement, for example, SO<sub>x</sub>, etc.

#### **Reference literature**

[55, UK EA, 2001], [121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004]

### **4.1.4. Precipitation of metals**

#### **Description**

The objective of these techniques is to precipitate the metals contained within aqueous wastes. Some techniques include:

- a. acidifying the waste to solubilise all the metals in a first step
- b. adjusting the pH to the point of minimum solubility where the metals will precipitate
- c. allowing the resulting treated waste to clarify by decantation when possible (for example, high concentrations of metals in water are very difficult to be clarified by decantation), and/or by the addition of other dewatering equipment (e.g. filter press or centrifuge equipment)
- d. avoiding the input of complexing agents, chromates and cyanides (due to the danger of HCN formation from acidifying waste materials)
- e. changing precipitation conditions, for example, if the target metal concentration of treated waste water is not achieved using hydroxide precipitation (e.g. because of the presence of complexing agents), sulphidic precipitation (e.g. with sodium sulphide or organic sulphides) can be used. This aims at the formation of metal sulphides which are difficult to dissolve in water. Hydrogen sulphide is used, and therefore operating conditions and emissions demand particular consideration. In practice, sulphide precipitation is used in treating waste water containing complexing agents
- f. avoiding organic materials from entering the process, since they generally disrupt the precipitation reaction
- g. organising the process according to the following steps:
  - experimental investigation by the laboratory; determination of a treatment programme
  - establishing process control values, e.g. pH value, temperature, metal concentration
  - determination of ancillary agents according to type, quantity, concentration
  - determination of dosage for the ancillary agents, e.g. l/h
  - determination of the sequence for the addition of the ancillary agents
  - functional testing of the equipment
  - execution of the precipitation/flocculation; documentation of process control.

#### **Achieved environmental benefits**

Substances such as chromium, zinc, nickel, lead are usually present dissolved in solution or absorbed onto particulate or colloidal matter. It is a relatively simple and robust technology and shows performances of up to 95 %.

#### **Cross-media effects**

Chromium (III), zinc and cadmium are amphoteric and solubility will rise at a pH above their minimum solubility points. The production of sludge containing metals can be seen as a cross-media effect. The amount

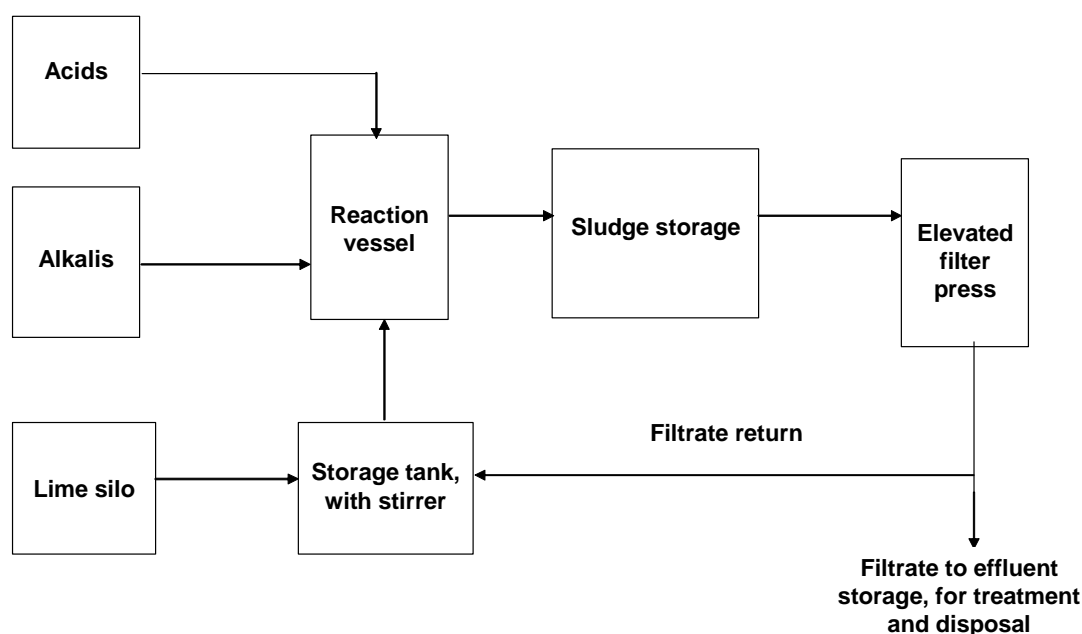
of filter cake can be reduced by replacing the lime by sodium hydroxide, however, in such a case, the fluorides are not precipitated.

The use of sulphide technique e (from the description section above) typically results in a high sulphide concentration of the waste water. Alternatively, wet oxidation or separation at source may be applied.

#### Operational data

Similarly to acid/alkali neutralisation, the process involves the addition of acid or alkali (which may be a waste) within a stirred reaction vessel. Typically lime is used as the hydroxide.

Related to technique b from the description section above, Table 3.13 (in Chapter 3) showed the pH range values for the precipitation of various metals as hydroxides. The pH value for minimum solubility depends on the metal, and then in the case of a mixture of metals, an optimum value needs to be found. For such an optimum pH, it may be that some metals do not precipitate at all. This is the reason why, in some cases, more than one pH step is used to maximise the removal of metals.



**Figure 4.1:** Representation of a precipitation/neutralisation process  
[55, UK EA, 2001]

The advantages of batch operations in the treatment of waste with characteristics which vary very much from load to load are shown by the results of the operation and experience, for example:

- for a constant pH value, the metal concentration in the waste water can still decrease
- by repeated mixing of waste water and sedimentary sludge, additional co-precipitation effects can be achieved; a prerequisite for co-precipitation is gentle sludge circulation and transport.



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Since in general metal corrosive materials are used, the plant (containers, pipelines, measuring technology) must be appropriately equipped and/or protected (use of synthetic materials, painting, etc.).

#### **Applicability**

Aqueous waste treatment processes treat a variety of compatible aqueous waste materials by precipitating soluble metals and acidic anions out of solution while increasing the particle size of suspended solids, thereby aiding later phase separation between solids and liquids by clarification and filtration. Typical wastes include interceptor wastes, paint spray booth wastes and process effluents, among others.

#### **Driving force for implementation**

In the Netherlands, this technique of concentrating metals in the sludge is applicable for waste waters containing metals (except for picking acid and except for waste waters containing precious metals) when the waste water contains a metal (As, Co, Cr, Cu, Fe, Mo, Ni, Pb, Sn, V and Zn) concentration of more than 200 mg/l of which 25 mg/l are present in the water fraction and / or the amount of Cd is bigger than 0.2 mg/l.

#### **Example plants**

In an example plant, galvanising/pickling acid is added to a reaction vessel, lowering the pH to 5. This allows the release of ferrous ions from the acid, to act as a reducing agent, reducing metals from high to low oxidation states, which can then be removed (as hydroxides) from solution by later increasing the pH to 9 by lime addition.

#### **Reference literature**

[55, UK EA, 2001], [86, TWG, 2003], [121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004], [153, TWG, 2005]

### **4.1.5. Break-up of emulsions**

#### **Description**

Some techniques include:

- a. using waste acids and waste alkalis as materials to break up the emulsions
- b. using evaporation, ultrafiltration or organic breaking up agents
- c. testing for the presence of cyanides in the emulsions to be treated. If cyanides are present the emulsions need a special pretreatment first
- d. setting up simulated laboratory tests first. The operator typically sets up a treatment programme, containing details about the type and quantity of the acids, caustic solutions and flocculation agents to be used. Laboratory tests on samples can help determine whether an adequate waste water quality can be achieved
- e. carrying out the process with substantial precision and control of the process and organic splitting.

#### **Achieved environmental benefits**

The acid splitting of emulsions is of extraordinary importance for the disposal of waste and for the protection of water, because waste, such as spent acids and waste alkali, can be used for the treatment of the emulsions. During organic splitting, incomplete splitting is possible in the event of underdosing, and a new formation of emulsions is possible with overdosing.

Techniques mentioned in the description section above are important to be considered in the determination of the the most appropriate method for the break-up of each type of emulsion to avoid environmental and operational problems.

#### **Cross-media effects**

Further treatment of the waste water may possibly be necessary subsequent to the treatment of the emulsion, for example using an ion exchange, or activated carbon adsorption. If this is necessary it should be specified as an operating instruction in the treatment programme.

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The use of waste acids and waste alkalis (see technique a in the description section above) typically produce a waste water with higher concentrations of salts and remaining oil. The oily sludge is typically more difficult to be landfilled and the oil cannot be recovered.

#### **Operational data**

The actual treatment of the emulsion, also referred to as splitting the emulsion, consists of two treatment phases:

- destabilisation (separation) of the emulsion, by mixing the emulsion with acids
- flocculation and precipitation of the dissolved metals present in the separated emulsion.

#### **Reference literature**

[121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004]

### **4.1.6. Oxidation/reduction**

#### **Description**

Some techniques include:

- a. abating the air emissions generated during oxidation/reduction
- b. having in place safety measures and gas detectors (e.g. suitable for detecting HCN, H<sub>2</sub>S, NO<sub>x</sub>).

#### **Achieved environmental benefits**

Reduces the emissions that may occur from the redox reactions.

#### **Example plants**

The collection of the exhaust air is ensured by suction with a fan and exhaust air filter. Here no measurements are made since the transported exhaust air rate is overdimensioned. The filter, which may involve acid or base scrubbers, is regularly controlled and if necessary regenerated.

#### **Reference literature**

[121, Schmidt and Institute for environmental and waste management, 2002]

### **4.1.7. Techniques for the treatment of wastes containing cyanides**

#### **Description**

Cyanides can be destroyed by using different kinds of oxidising agents, such as hypochlorite, chlorine, ozone, peroxides and peroxides with UV radiation. Other techniques can be electrochemical oxidation or wet oxidation with air (medium to high pressure). High temperatures also destroy cyanides in solid waste. However, incineration techniques are not included in this document. Some issues to consider include:

- a. cyanides can be destroyed in aqueous waste streams by oxidation with a basic oxidising agent at a pH not less than 10 and a chlorine concentration of less than 1 g/l. The reaction is very rapid
- b. adding caustic soda in excess can prevent the pH from falling too low
- c. the mixing of cyanide wastes with acidic compounds (e.g. neutralisation, acid emulsion break-up) needs to be avoided
- d. since the treatment of cyanide is by oxidation the destruction can be checked by the measurement of redox potentials (electropotentials). The addition of sodium hypochlorite to an effluent sump can therefore be controlled
- e. the use of electrolysis to oxidise cyanide.

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#### **Achieved environmental benefits**

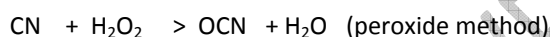
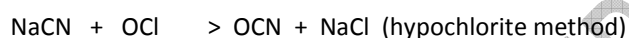
The resulting cyanate cannot readily be reduced back to cyanide and any discharge of cyanate to a watercourse will not lead to free cyanide being generated. There are also less health risks. The pretreatment of waste waters containing cyanides is essential to avoid the formation of metal-cyanide complexes. With these techniques, concentrations of less than 0.1 mg/l of cyanide can be achieved.

#### **Cross-media effects**

Use of oxidant (e.g. hypochlorite, potassium permanganate) when required.

Using hypochlorite or chlorine increase the salt content of the waste water and can also increase the content of AOXs. Cyanogen chloride may also be generated during the treatment with chlorine oxidisers. When using chlorinated oxidisers, it is important that the pH of the system remains greater than 10. If the pH is too low, then cyanogen chloride and hydrogen cyanide can be formed. If there is excess hypochlorite present then chlorine gas can be released, and if there is a lack of hypochlorite then residual cyanide will present.

Using H<sub>2</sub>O<sub>2</sub> or ozone as an oxidiser does not create any of the by-products as shown in the following reactions:



#### **Operational data**

Discharges of aqueous effluents to watercourses is monitored continuously for cyanide content, free chlorine and the pH level. The use of pure oxygen as an oxidiser is not as efficient as the other oxidants mentioned.

#### **Applicability**

Chemical and thermal treatment methods are most widely used for the destruction of waste streams containing cyanide.

#### **Driving force for implementation**

The destruction of cyanides.

#### **Reference literature**

[55, UK EA, 2001], [86, TWG, 2003], [121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004], [156, VROM, 2004]

### **4.1.8. Techniques for the treatment of wastes containing chromium (VI) compounds**

#### **Description**

Some techniques include:

- the mixing chromium (VI) wastes with other wastes needs to be avoided
- the conversion of Cr(VI) to less hazardous Cr(III) can be achieved by the addition of a reducing agent, for example, sodium metabisulphite, pickling acid, sodium dithionite. The trivalent metal can then be precipitated in the normal way (see Section 4.1.4).

#### **Achieved environmental benefits**

Chromium (VI) is the highest oxidation state of the metal, an example of this is chromic acid, or chromium oxide (CrO<sub>3</sub>) which is acidic, toxic, water-soluble and used as an oxidising agent. With these treatments concentrations less than 0.1 mg/l of chromium (VI) are achievable.

#### **Cross-media effects**

There is a need for a reducing agent.

#### **Driving force for implementation**

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Treatment by straightforward neutralisation of chromium (VI) compounds is ineffective so an initial step needs to be applied involving reduction to chromium (III), the trivalent state.

**Reference literature**

[55, UK EA, 2001], [121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004], [156, VROM, 2004]

#### **4.1.9. Techniques when treating waste water contaminated with nitrites**

**Description**

Some techniques include:

- a. avoiding mixing nitrites wastes with other wastes
- b. checking and avoiding nitrous fumes during the oxidation and acidification of nitrites
- c. checking and avoiding nitrous fumes during the reduction of nitrites.

**Achieved environmental benefits**

Concentrations of less than 2.0 mg/l of nitrite can be achieved by good optimisation of the nitrites treatment process.

**Cross-media effects**

Use of an oxidiser agent is required in oxidation processes. Reducing agents used are urea or amidosulphuric acid.

**Example plants**

There are three plants operating such systems in Austria.

**Reference literature**

[121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004]

#### **4.1.10. Treatments of phenolic solutions by oxidation**

**Description**

It is possible to treat aqueous wastes containing phenol (3 – 5 w/w-%) by catalytic oxidation, using an oxidising agent and a metal catalyst or by a strong oxidising reagent (e.g.  $\text{KMnO}_4$ ).

**Achieved environmental benefits**

Reduces the phenol content in aqueous wastes.

**Cross-media effects**

Use of oxidising agent and catalyst where necessary.

**Operational data**

The treatment procedure needs to take account of the exothermic nature of the reaction. Feedstocks can be diluted before treatment. The process temperature, pH and redox potential are continually monitored.

**Example plants**

An example plant in UK shows uses of this process on a three tonne batch basis in a stainless steel, double skinned vessel.

**Reference literature**

[55, UK EA, 2001], [150, TWG, 2004]

#### **4.1.11. Techniques for wastes containing ammonia**

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### **Description**

Some techniques include:

- a. for waste with ammonia solutions up to 20 w/w-%, treating them using a dual column air stripping system with an acidic scrubber. A dual column process has been developed, where the initial column raises the temperature of the feedstock and maintains the pH between 10 – 11. The feedstock is then transferred to a second column where it is run countercurrently across a packed column against air
- b. recovering the ammonia in the scrubbers and returning it to the process prior to the settlement stage
- c. removing the ammonia removed in the gas phase by scrubbing the waste with sulphuric acid to produce ammonium sulphate.

### **Achieved environmental benefits**

These techniques prevent a large emission of ammonia gas during the initial neutralisation process when the pH is changing rapidly, as the tanks are agitated and the temperature is rising.

### **Operational data**

Solutions high in ammonia can also undergo pretreatment (e.g. air stripping) to reduce the concentration of ammonia before reaching the treatment plant.

### **Applicability**

Such systems are applied to waste waters with a high ammonia content. There are other wastes containing ammonia / ammonium what, e.g. landfill leachate, for which the described stripping system is not adequate due to the transfer of other substances to the gas phase.

### **Economics**

The solutions containing ammonia can also be used as a deNO<sub>x</sub> agent. This destination might be less expensive than collection/treatment as a hazardous waste.

### **Driving force for implementation**

Ammonia contributes to acid rain and manure pollution.

### **Reference literature**

[55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [150, TWG, 2004]

## **4.1.12. Filtration**

### **Description**

Some techniques include:

- a. extending any air sampling for ammonia in exhaust stacks or filter press areas to cover VOCs
- b. linking the air space above some presses to the main abatement system at the plant
- c. improving the draining behaviour of mud by the addition of flocculation agents, for example lime, or synthetic flocculation agents. This conditioning of the mud take place in containers equipped with adjustable agitators. To mix the mud with the flocculation agents, an intensive mixture can be achieved in a short time by accelerating the agitator; the agitator usually moves slowly during the floc formation, so as not to impair flocculation.

### **Achieved environmental benefits**

Improves the filtration process and reduces the fugitive emissions. Filter cake with high concentrations of metals, e.g. nickel and copper, can be used as a raw material in the metalurgical industry.

### **Cross-media effects**

The need to clean the filter cloths is a disadvantage; applying high pressure cleaners with water or washing the cloths in special partly acid washing solutions have proven to be beneficial for this purpose.

The need to maintain the presses and to remove cake/sludge means that the system is opened on a regular basis, making it hard to avoid air emissions.

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**Operational data**

Energy is required to run the process.

**Reference literature**

[55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004]

### 4.1.13. Flotation

**Description**

The dissolved air flotation (DAF) system generates a supersaturated solution of waste water and compressed air by raising the pressure of the waste water stream to that of the compressed air, then mixing the two in a retention tank. This supersaturated mixture of air and waste water flows to a large flotation tank where the pressure is released, thereby generating numerous small air bubbles. Through a combination of adsorption and entrapment, the flocculated particles rise to the surface of the reactor. The suspended solids float to the top of the liquid and form a foam that is then skimmed off. Some soluble colloidal substances are removed from the waste water by adding coagulation and flocculation chemicals to form precipitates with the solutes.

**Achieved environmental benefits**

DAF is widely used because of its effectiveness in removing a range of solids.

**Cross-media effects**

Emissions to the air are possible and a large amount of chemical sludge is produced (containing  $\text{FeCl}_3$ ,  $\text{Al}(\text{OH})_3$ , polyelectrolytes and enclosed particles), which need to be treated before disposal.

**Operational data**

Usually chemicals such as polymers, polyelectrolytes, aluminium salts (e.g. sulphates), or iron salts (e.g. ferric chloride) are used to enhance the adhesion of bubbles. The process requires energy to run.

**Driving force for implementation**

No need for a sedimentation vessel.

**Example plants**

DAF is widely used.

**Reference literature**

[55, UK EA, 2001], [86, TWG, 2003], [150, TWG, 2004]

### 4.1.14. Ion exchange processes

**Description**

Some techniques include:

- using ion exchangers only for salt concentrations of less than 1500 mg/l. Otherwise the treatment is not economically viable
- using pretreatments to reduce the salt concentration, e.g. precipitation
- removing solid materials in solutions by sand filters or activated carbon adsorption before using ion exchange processes
- using conductivity measurements to monitor and operate the ion exchanger plant (cation-anion combination). It is very sensitive and not likely to be susceptible to interference.

Further test parameters may be oils, emulsified materials (combustion loss), solid materials in the intake of the ion exchanger, the pH value, aromatic hydrocarbons, chlorinated hydrocarbons and organic acids.

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**Achieved environmental benefits**

Improvement of the ion exchange processes.

**Operational data**

Ion exchangers can only work in 'clean' solutions, i.e. solutions, which primarily contain ions but no solid constituents.

**Reference literature**

[121, Schmidt and Institute for environmental and waste management, 2002]

### 4.1.15. Membrane filtration

**Description**

The requirement for resistance vis-a-vis cleaning, long life as well as low manufacturing costs of the membranes, applies to all membrane procedures. The selection of the suitable membrane is of central importance for the treatment of waste. Some techniques in the selection and use of a suitable membrane include:

- a. examining in the laboratory which membrane is suitable for the waste to be treated
- b. submitting the permeate and concentrate resulting from ultrafiltration to subsequent treatment. In the case of the permeate, this may be detoxification, neutralisation, precipitation or evaporation. In the case of the concentrate, this may need to be disposed of
- c. monitoring the following parameters in micro and/or ultrafiltration systems:
  - pH value
  - throughput
  - electrical conductivity
  - pressure, temperature
  - oil content
  - permeate efficiency and/or quality (e.g. clouding value, hydrocarbons)
  - cyanide, nitrite, chromate
  - solid content.

**Achieved environmental benefits**

Some benefits include:

- no chemical additive needed (no material conversion)
- no additional waste water contamination by chemicals (no salination).

**Cross-media effects**

Energy requirements for the process.

**Operational data**

It is possible to automate the filtration of membrane. Also, these filtration units require little space.

**Applicability**

Membrane procedures are suitable for the treatment of waste if the waste is pretreated, or if it involves defined waste with a proven suitability for membrane filtration. The materials giving rise to unfavourable changes in the membranes, such as adhesion or, swelling of the membrane, must be separated. Bearing these constraints in mind, membrane filtration is:

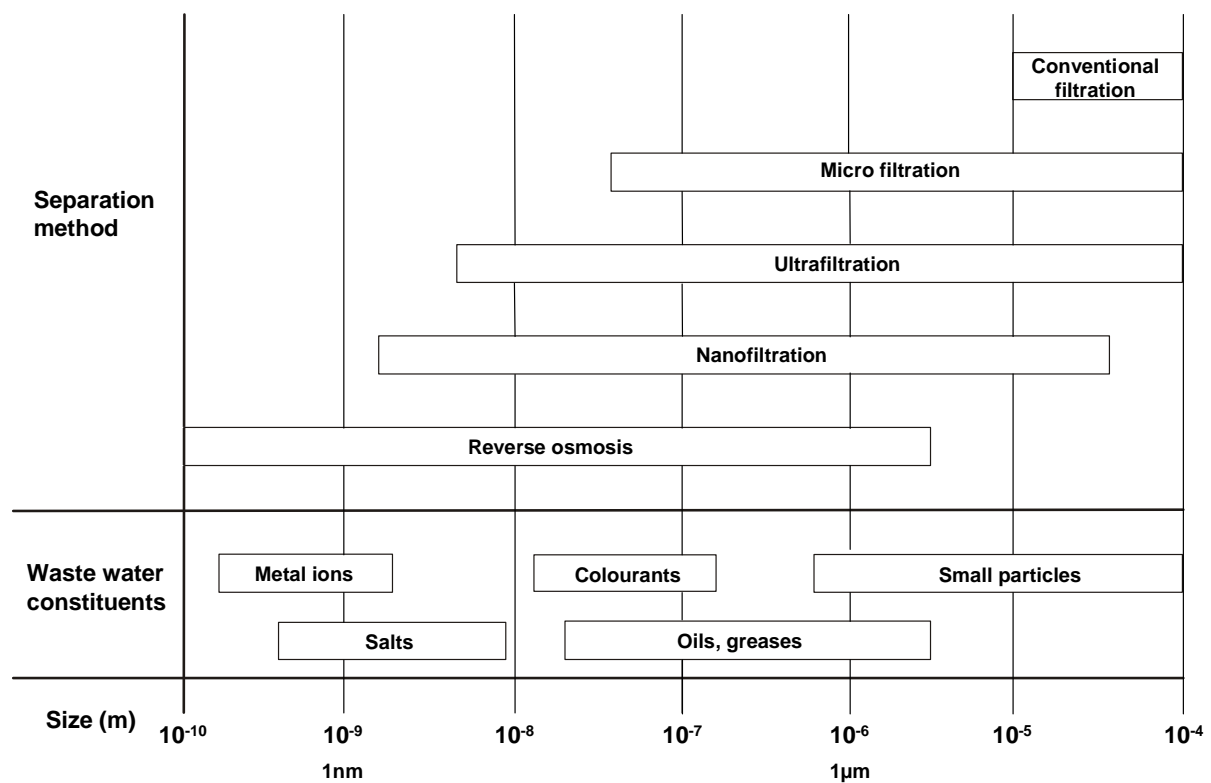
- suitable both for high and low-charged waste water
- usable in emulsion separation, independently of type, concentration or stability.

Type of substance	Effect on the membrane	Technique to overcome the problem in the membrane
Solids with grain size >0.5 mm	Blockage, wear of the	Suitable with a pre-purification

	membrane	stage
Solvents	Swelling of the membrane, structural change, permeability reduces	Prevent introduction
Alkali solutions and acids with extreme pH values	Possible destruction of the membrane material	Adjust pH value
Organic materials (with cellulose acetate membranes)	Membrane damage by rot	By means of bactericides
Silicone (from 0.1 %)	Blockage of membrane	Prevent introduction into the membrane
Free oil (from 1.0 %)	Blocking of membrane <sup>1</sup>	Prevent introduction into the membrane
<sup>1</sup> Use of RO and possibly NF with 1 % oil levels will not work effectively over an extended operational period without very extensive pretreatments.		

**Table 4.1: Techniques to consider in membrane technology**  
[121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004]

In principle, membrane technology can be used for the purposes shown in Figure 4.2:



**Figure 4.2: Classification of membrane technology by the separation task**  
[121, Schmidt and Institute for environmental and waste management, 2002]

#### Economics

Because it is typically automatised, staffing costs are low.

#### Reference literature

[121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004]



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#### 4.1.16. Sedimentation

##### Description

Settlement is carried out in clarifiers that need to be specifically designed with an inlet, outlet, settling zone and sludge blanket (or sludge zone). The addition of flocculation agents to the sludge and waste water to be treated is recommended to accelerate the sedimentation process and to facilitate the further separation of solids.

##### Achieved environmental benefits

Increases the sedimentation efficiency. Sedimentation of solids generally simplifies the waste treatment procedures which follow. To this extent, in the right part of the process, sedimentation is an advantage in the treatment of waste in Ph-c plants. However, unintentional sedimentation processes, e.g. in reaction containers, are a disadvantage since processes can be affected and often the build-up of sediment can only be removed at considerable expense.

##### Cross-media effects

Creation, typically, of a residue. The addition of flocculants implies that they will either appear in the treated waste water or they will be present in the separated solid.

##### Operational data

The efficiency of the sedimentation process is affected by the waste water and suspended solids characteristics and by variations in the flow and general operation. In practice, the following sedimentation agents have proven to be beneficial:

- milk of lime  $\text{Ca}(\text{OH})_2$
- iron (III) chloride  $\text{FeCl}_3$
- polyelectrolytes.

##### Applicability

The solids may be discrete suspended particles that are self-settling, or there may be a range of sizes and surface characteristics, which then require the formation of flocculating suspensions to coagulate and settle the mass, i.e. through chemical conditioning. In certain cases, it is not necessary to use flocculation agents because solids are self-settling or because they are not effective.

##### Economics

Applying this technique allows savings to be made on the discharge and transport costs, since only the sediment needs to be managed and not the total aqueous suspension.

##### Example plants

Paper mills (sedimentation of the cellulose fibres that are too short) and other plants with high content in suspended solids in the waste waters.

##### Reference literature

[55, UK EA, 2001], [86, TWG, 2003], [121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004]

#### 4.1.17. Sieving

##### Description

See Section 2.2. Some techniques for sieving operations include:

- 
- a. avoiding overload of the sieving equipment (either optically by monitoring the equipment controls or automatically by blocking out the filler pump by means of the level indicator storage container's)
  - b. correctly cleaning the filter apertures as required (optical, empirical). Some good cleaning measures include applying rapid cleaning and steam or high pressure water jetting
  - c. ensuring that there is an unimpaired discharge of filter underflow and overflow at all times (through use of optical, filler pump shut-off mechanisms or other control).

#### **Achieved environmental benefits**

The sieving of waste is performed as an initial treatment procedure. The separation out of particles which may harm equipment, processes or products is beneficial for all successive waste treatment measures.

#### **Operational data**

The advantages of sieves are in their simple, robust construction, their low maintenance needs and the fact that they are user friendly, and offer good reliability. The disadvantages are generally caused by the wastes themselves, e.g. clogging of the filter apertures can occur as the result of the degree of viscosity of liquid waste, which then impedes separation.

#### **Reference literature**

[121, Schmidt and Institute for environmental and waste management, 2002]

### **4.1.18. Solvent extraction**

#### **Description**

Some techniques include:

- a. using well operated and regulated processes
- b. returning the extraction solvent for re-use in a closed loop
- c. using anti-foaming agents when faults occur in the extraction due to surface-active substances (e.g. tensides) resulting from the mixing processes
- d. avoiding using solvents with comparable chemical characteristics to the component to be extracted, in order to avoid poor separation effects, e.g. azeotropic mixtures
- e. improving the separative performance during extraction by increasing the temperature
- f. separating substances which may have negative effects in pretreatment procedures.

#### **Achieved environmental benefits**

Enhances the environmental performance of the solvent extraction. Some reasons for using extraction include: its low energy consumption for the separation of substances, from low concentrated waste water up to the ppm range; the possibility of extracting insoluble substances, and also the high level of selectivity that can be achieved by using reactive components and suitable extracting agents during the extraction process.

#### **Cross-media effects**

Emissions of VOCs to the air.

#### **Economics**

There is a saving of raw material and transport costs if the distillation can be performed on site.

#### **Example plants**

Many systems return the extraction solvent for re-use in a closed loop.

#### **Reference literature**

[55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [121, Schmidt and Institute for environmental and waste management, 2002], [150, TWG, 2004]

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#### 4.1.19. Techniques when treating waste water containing precious metals

##### Description

Photographic liquid waste contains several toxic and not easily degradable compounds. By means of physico-chemical and biological treatment, including evaporation, the diffusion of these compounds to the environment is minimised. Some techniques are:

- a. for black and white photographic waste water, recovery of metals if the concentration of silver is greater than 50 mg/l, and purification is followed by evaporation and incineration of the concentrate in a grate furnace or cement kiln
- b. for colour photographic waste water, recovery of metals if the concentration of silver is greater than 100 mg/l and purification is followed by evaporation and incineration of the concentrate in a grate furnace or cement kiln.

##### Achieved environmental benefits

In comparison with detoxification, neutralisation and dewatering for the removal of metals by means of chemicals, there is a reduction in the consumption of chemicals and the sludge produced.

##### Cross-media effects

In comparison with a detoxification, neutralisation and dewatering for the removal of metals by means of chemicals, the consumption of energy is increased, e.g:

- electricity for the electrolysis
- heat for the evaporation.

##### Operational data

Sulphide precipitation and ultrafiltration generates sulphide sludge at approximately 5 to 10 kg/m<sup>3</sup> liquid photo processing waste water. From the sludge, silver and other metals are recovered in pyrometallurgic processes which generate slags as a residue. The physico-chemical and biological treatment of the desilvered photographic waste water generates sludge at approximately 0.1 to 0.2 t/t waste water.

Silver is recovered for re-use and concentrations of silver and other metals in the waste water are reduced. The recovery of silver is approximately 95 %. The silver content in the permeate of membrane filtration is <1 mg/l in the case of black and white photo processing waste water and <10 mg/l in the case of colour photo processing waste water.

##### Applicability

The techniques for recovery of metals are not only applicable to photographic waste waters, but also to other waste waters containing (precious) metals, e.g. the galvanic industry. Electrolysis gives a higher yield and costs less energy as metals are more precious and concentrations are higher. The capacity of one of the example plants for metal recovery ranges from 10 to 20 kt/yr.

The physico-chemical and biological treatment techniques for desilvered photographic liquid waste waters are applicable for similar waste waters. **Error! Reference source not found.** shows the acceptance criteria for desilvered photographic liquid waste and similar waste waters (with the same processing path). The capacity of one of the example plants for physico-chemical and biological treatment is approximately 100 to 200 kt/yr.

##### Driving force for implementation

Effluent standards based on the Surface waters Pollution Act.

##### Example plants

Two example plants in the Netherlands.

##### Reference literature

[150, TWG, 2004], [156, VROM, 2004]

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#### 4.1.20. Techniques for the treatment of aqueous marine waste

##### Description

The treatment of aqueous marine wastes can be distinguished between waste waters containing oil and waste waters containing chemicals. Some techniques are:

- a. applying specific pretreatment processes in the case of waste waters containing metals (see Section 4.1.19 above)
- b. applying physico-chemical pretreatment and a biological treatment in the case of waste waters containing oil
- c. treating the exhaust gases to reduce the VOC and odour emissions
- d. defining acceptance and processing standards (maximum concentrations in the waste) for every treatment route
- e. separating oils / chemicals, water and sludge
- f. preparing the oil or chemical fraction for use as fuel if suitable
- g. applying standards (maximum concentrations) for mixing wastes to be used as fuel
- h. not mixing or diluting waste waters to meet effluent standards
- i. dewatering the sludge and, if suitable, applying a thermal treatment for material re-use
- j. treating the waste water.

##### Achieved environmental benefits

Compared to the discharge of untreated waste water or merely biological treatment, the described techniques reduce emissions of contaminants to surface waters.

##### Cross-media effects

- production of a sludge that has to be disposed of or undergo further treatment
- consumption of chemicals
- consumption of energy
- emissions to the air, e.g. VOC and odour.

##### Operational data

The removal efficiencies of flocculation/flotation and aerobic biological treatments by a waste water treatment installation are presented in Table 4.2:

Component	Removal efficiency flocculation/flotation (%)	Removal efficiency aerobic biological treatment (%)	Waste water treatment Total efficiency (%) <sup>2</sup>
Suspended particles	>99	-	>99
Oil	>99 <sup>1</sup>	99	>99
COD	20	85	88
Phenols	-	99	99
Total N (Kjeldahl)	-	50	50
P	-	50	50
BTEX	75	99	99.7
PAHs	96	95	99
CN	-	75	75
EOX + VOX	30	97	98
EOX	85	85	98
Heavy metals	80	-	80
Cd	80	-	80
Hg	>90	-	>80
<sup>1</sup> removal of oil layer			
<sup>2</sup> total of flocculation/flotation and biological treatments			

**Table 4.2: Removal efficiencies of flocculation/flotation and biological treatment of waste water**

Emissions of VOC to the air are released from tanks during storage and transfer, from treatment installations and from seal leakages. Emissions can be reduced by enclosed installations, inspection and maintenance to avoid leakages.

Treatment of the exhaust gases by filtering, scrubbing or incineration can reduce these emissions. A biofilter or activated carbon filter may be applied to prevent the emissions of VOC and odour. An alternative for reducing these emissions is aeration with oxygen instead of air. This reduces the flowrate of the air input and the exhaust gas. The disadvantages are the higher consumption of oxygen and the higher consumption of pumping energy to compensate the reduction of the mixing due to the fact that less air is blown in.

If exhaust gas treatment is applied, emissions vary from approximately 0.01 kg/m<sup>3</sup> waste water in the case of incineration, with an efficiency of 99.9 %, to 0.05 kg/m<sup>3</sup> waste water in the case of a wet scrubber.

#### Applicability

The capacities of the example installations range from 200 to 500 kt/yr.

#### Driving force for implementation

Effluent standards based on the Surface Waters Pollution Act in the Netherlands.

#### Example plants

Three example plants in the Netherlands.

#### Reference literature

[150, TWG, 2004], [156, VROM, 2004]

### 4.1.21. Abatement techniques applied in Ph-c treatment plants

Table 4.3 shows the air abatement techniques applied in Ph-c treatment plants

Installation	Offgas treatment for the treatment area/ reactors <sup>a)</sup>	Air abatement/off-gas treatment in storage areas
Solidification	Bag filter	Bag filter
Multifunctional Ph-c installation	Scrubber for acids Scrubber for NH <sub>3</sub> in operation, if necessary	n.a.
Multifunctional Ph-c installation	Scrubber for acids Oxidising scrubber	Carbon filter for some tanks containing oily waste
Multifunctional Ph-c installation	Off-gas is used during the incineration of hazardous waste	n.a.
Multifunctional Ph-c installation	4- to 5-step treatment system: Water scrubber (eliminating aerosols containing oil and dust) Scrubber for acids Scrubber for NH <sub>3</sub> Biofilter, closed system Carbon filter in operation, if necessary	Ventilation for the whole plant, treatment of the off-gas
Multifunctional Ph-c installation	Scrubber for NH <sub>3</sub> Biofilter	Biofilter
Multifunctional Ph-c installation	Scrubber for acids Scrubber for NH <sub>3</sub>	Ventilation
Multifunctional Ph-c installation	Scrubber in operation during cyanide or nitrite oxidation	Ventilation
Multifunctional Ph-c installation	Scrubber for acids Oxidising scrubber Biofilter for the organic part	Biofilter together with off-gas of biological treatment of MSW
Multifunctional Ph-c installation	Scrubber for acids Scrubber for NH <sub>3</sub> Biofilter (closed system) Off-gas funnel	Biofilter
Soil washing / attrition plant	1-step scrubber	n.a.
<sup>a)</sup> the air n.a	Many plants use the scrubbers only during Ph-c treatment in the reaction vessel. Other plants operate abatement system continuously. no information available	

**Table 4.3: Off-gas treatment in large Ph-c installations in Austria  
[150, TWG, 2004]**

Next Figure 4.3 and Table 4.4 shows the air abatement systems of a Austrian plant and the waste water parameters achieved after biological treatment of the waste waters.

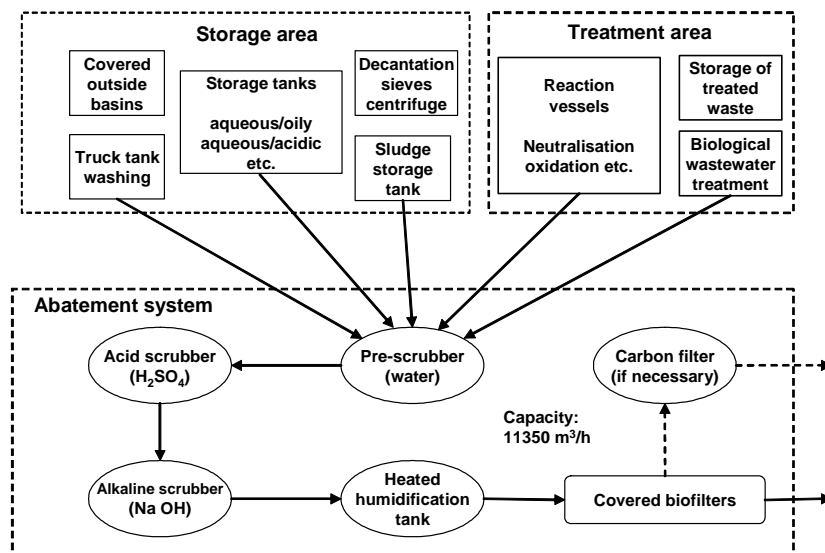


Figure 4.3: Air control and abatement system of a Ph-c plant  
[150, TWG, 2004]

Parameter	Feed (primary effluent) (mg/l)		Effluent after biological treatment (sequential batch reactor) (mg/l)	
	Minimum	Maximum	Minimum	Maximum
COD	2500	12000	600	1500
NH <sub>4</sub> -N <sup>a)</sup>	25	16000	<1	150
Nitrite	10	300	<1	<1
Nitrate	10	1000	<1	<1
Phenols	10	500	<2	<2
Oil content	--	--	<0.5	--

a) Effluent after biological treatment: Often around 20 mg/l

Table 4.4: Effluent concentration of an Austrian plant before and after tertiary waste water treatment (on-site sequential batch biological treatment)  
[150, TWG, 2004]

## 4.2. Techniques for the physico-chemical treatments of solids and sludges

### 4.2.1. Pretreatment before immobilisation

Description

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Pretreatment before immobilisation basically consists of washing/leaching of salts with water, and the physico-chemical pretreatment of metals (especially insolubilisation of the amphoteric metals). The subsequent treatment, solidification, is not covered in this Section.

#### **Achieved environmental benefits**

This treatment produces a filter cake with a reduced toxicity and solubility and salted water. It helps to reduce the leachability of the waste OUT and contamination by the leaching out of soluble compounds.

#### **Operational data**

The process is more sophisticated than the simple solidification one.

#### **Applicability**

Waste containing chromates, amphoteric metals such as Pb and Zn and waste with some soluble salts content typically need pretreatment before being subjected to the immobilisation process. This pretreatment allows the treatment of fly ashes and salts arising from the dechlorination of fumes in household waste incineration. It can also be applied to the fly ash resulting from both lime treatment of the fumes and from the bicarbonate of soda treatment. In the latter case (sodium bicarbonate), it dissociates the soluble and non-soluble solid components, and reduces the amount of disposal in landfills by recycling the soluble salts in a soda ash factory.

#### **Economics**

The investment cost is higher than for a solidification process alone.

#### **Example plants**

This is already applied in a large scale factory in France treating 1000 tonnes per year of fly ash produced in France.

#### **Reference literature**

[136, Straetmans, 2003], [150, TWG, 2004]

## **4.2.2. Laboratory activities**

#### **Description**

Some techniques regarding laboratory activities include:

- a. having the laboratory on site
- b. applying quality control (to include leachability tests and compressive strength, i.e. for solidification processes), including screening each proposed waste to ensure any wastes containing process inhibitors are excluded. In the case where inhibitors are present, see technique c below. For each waste stream, laboratory scale testing should be carried out to maximise the effectiveness of the mix and the quantity of the absorbents/binders to be added, and to identify an optimum 'formula' to be used in later full scale treatment should the waste stream in question be found suitable. Any such testing should take into account the effects of different waste streams being treated in the same batch and in addition identify a minimum residence time within the reaction vessel. Records of which waste streams have already been tested should be kept, showing whether they have been accepted or rejected as suitable for treatment by the process (see Section **Error! Reference source not found.**)
- c. addressing any inhibitors identified in the binder formulation with secondary binders/additives. The key issue is to confirm this to be the case by conducting treatability studies for each waste stream
- d. specifying the length of time that samples need to be kept available for analysis. This needs to include a reference to the length of time taken to achieve full stability (see Cross-media Section below) of the end-product
- e. demonstrating how batch non conformance waste will be dealt with
- f. testing the leachability of inorganic compounds, using the standardised CEN leaching procedures and applying the appropriate testing level: basic characterisation, compliance testing or on-site verification
- g. conducting acceptance procedures when waste arrives at the installation, including leachability tests on every load prior to treatment, to confirm the levels of key indicator substances identified at the pre-acceptance stage



- 
- h. analysing the following group of compounds that may cause landfilling problems: Cl, CN, F, sulphates, hydrocarbons, PAH, PCB, phenols, As, Cd, Cr total, Cr(VI), Hg, Ni, Pb, Zn.

#### **Achieved environmental benefits**

An on-site laboratory forms the essential element in providing assurances that the necessary process input controls are in place and that a consistent waste OUT is generated.

#### **Cross-media effects**

Cement or lime-based systems may take years to stabilise and decades/centuries or even longer to achieve equilibrium with the local environment. Because of this, talk about full stability may be technically unrealistic.

#### **Applicability**

Related to technique f in the description section above, the physico-chemical treatments are applied to monolithic and granular material (e.g. treatment of bottom ash).

Related to technique g in the description section above, it is sometimes questioned if it is environmentally and economically justified to carry out a leach testing on every load prior to treatment in the case of well characterised waste streams or if there is a minimum on load size.

#### **Driving force for implementation**

Landfill Directive 1999/31/CE and the Council decision 2003/33/EC (CEN) relate to the parameters that should be considered to determine if a waste can be landfilled:

- Landfill Directive (1999/31/EC) specifies the principles of characterisation of waste before landfilling which are: a) application of the 3-step characterisation procedure (basic characterisation, compliance testing, on-site verification), and b) Annex II of the Landfill Directive states that the parameters of composition, leachability, long term behaviour and general properties of a waste to be landfilled need to be known as precisely as possible
- The CEN procedures specify under which conditions and which type of tests need to be used
- 2003/33/EC establishes criteria and procedures for the acceptance of waste at landfills. This also includes waste acceptance criteria, sampling and test methods.

Related to the application of technique h (from the description section above) in France, PAHs and PCBs are not systematically analysed before stabilisation. Analysing is only carried out when PAHs and PCBs are found in large quantities (which can be concluded from the origin of the waste).

#### **Reference literature**

[51, Inertec, et al., 2002], [55, UK EA, 2001], [86, TWG, 2003], [150, TWG, 2004]

### **4.2.3. Immobilisation**

#### **Description**

Some techniques include:

- a. defining an acceptable range of characteristics of a waste that can be effectively treated by the process. This range will be determined by the ability of the process to immobilise the chemical/ion in question, to ensure the final product can meet a defined specification
- b. using suitably designed reaction vessels for all immobilisation processes
- c. performing these processes within controlled reaction vessels. Given the degree of process control that is needed to ensure the correct ratios of waste and reagent/binder entering the process and that sufficient mixing (and residence time) is achieved, it is essential that such vessels achieve these objectives. Automated loading, charging and mixing devices which can be monitored and controlled, will also be required
- d. using suitable process monitoring within enclosed and abated systems
- e. applying pre-acceptance procedures to assess waste
- f. implementing measures to restrict dusty reagents

- 
- g. restricting wastes to those with low concentrations of VOCs or odorous components (see Applicability and Cross-media Sections below)
  - h. employing controlled and enclosed methods of charging
  - i. mixing reagents and waste using impellers or mixing systems integral to the mixing vessel
  - j. using screw feeders, gravity or pneumatic means for handling systems for bulk transfer of dry wastes and reagents
  - k. replacing the need to decant liquid wastes from drums and containers by utilising separate 'make-up' tanks to premix liquids and pumpable sludges
  - l. delivering the feedstock by pipe into the mixing vessel
  - m. using extraction systems designed to take into account the removal of the large volumes of air present due to the dimensions of the mixing areas and the need to have vehicular access for loading and unloading. It will also be necessary to demonstrate that the design of the extraction systems are capable of controlling all foreseeable emissions, other than in emergency situations
  - n. having a central abatement system in place to handle the flow of air, as well as the peak loadings associated with charging and unloading
  - o. detailing the methods of treatment and disposal of all spent scrubber liquors and absorbents, (for example, activated carbon and trapped emissions)
  - p. having a regular inspection and maintenance programme in place, including:
    - replacing the underground or partially underground vessels without secondary containment by aboveground structures
    - replacing structures without secondary containment
  - q. carrying out physico-chemical treatments, such as neutralisation reactions in the liquid phase, in order to enhance mixing and process control
  - r. guaranteeing that solid phase neutralisation reactions have been carried out to the completion of the reaction
  - s. using hydraulic binders complemented by specific chemical reagents, especially for:
    - mercury fixation as  $\text{HgS}$  and  $\text{Hg}_3(\text{SO}_4)_2$
    - fixation of metals as metallic hydroxide sludge (e.g. Zn, Pb, Cu, Cr, Cd) as insoluble compounds and by solidification
    - reduction of hexavalent chromium in basic conditions (e.g. by  $\text{FeSO}_4$ ), followed by precipitation and solidification
    - fixation of organic compounds from that sludge from the chemical industry containing sulphates and organic salts, followed by precipitation of sulphates to ensure the structure durability, for example by adding clay to adsorb organic compounds
    - a high arsenic content (e.g. from the chemical or metallurgical industry, or from ore treatment) by oxidation of As (III), followed by stabilisation and solidification
  - t. considering the possibility of increasing the final product quality by using additives (for example, hydrophobic reactants, etc.)
  - u. not solely relying on stabilisation processes for the disposal of intractable wastes which are difficult to treat and expensive to incinerate. These include solid cyanides, oxidising agents, chelating agents, high TOC wastes, wastes containing low flashpoint solvents and gas cylinders
  - v. restricting the amount of reagents (including chemical and physical binders and solidification reagents) that can be added to prevent dilution
  - w. having immobilisation specialist practised on demand using specialist binders developed in laboratory test for a specific waste stream.

#### **Achieved environmental benefits**

Enhances the environmental performance of immobilisation techniques (e.g. reduction of permeability, reduction of specific surface, chemical buffering). Stabilisation is a cold process and consequently does not require energy. The waste OUT of these techniques typically has very good physico-chemical/leaching characteristics. Because the process is a cold process, fumes or air pollution are minor (e.g. generated by the use of fuels). Water permeability of  $3.7 \cdot 10^{-11}$  m/s can be achieved in the final product when cement is used as immobiliser.

#### **Cross-media effects**

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Waste OUT/waste IN ratios range between 1.2 and 2.4 in weight and generally between 0.9 and 1.4 in volume (due to the typical increase of the density of the waste OUT compared with the waste IN). Thus, the process leads to an increase in weight and a minor change in volume.

In order to avoid VOC emissions (see technique g in the description section above), waste containing VOCs could be treated in an enclosed mixing vessel (e.g. pugmill), treating the emitted VOCs that are not solidified by e.g. scrubbers. Such secondary treatments may avoid double handling (e.g. thermal desorption to deal with VOCs followed by stabilisation/solidification to deal with metals).

Immobilisation is not able to reduce the content of any contaminant in the waste, only change the chemical composition by some chemical reactions. Organic wastes are typically not immobilised by stabilisation/solidification they are typically adsorbed by the solid matter. Whatever stabilisation/solidification finally reaches as a process, it is considered that the waste OUT is not stable for a long period of time and the compounds of the waste OUT may escape (e.g. leaching).

The probable increase of the pH and alkaline capacity of the mixture by this treatment can lead to an increase of the leaching properties for the amphoteric metals (for pH above 12.5 lead, cadmium), species sensitive to pH like arsenic and cyanides as well as some organic components.

#### **Operational data**

This technique is easy to use and is a relatively simple process. The energy consumption of the treatment is low. When cement is used as a stabilisation material the ratio of waste to be treated to the cement used is between 1:3 and 1:4, depending on the type of waste.

#### **Applicability**

These techniques are most likely to be effective in the treatment of inorganic wastes where solubility is already quite low. With this technique, a large range of waste can be treated (liquids, solids, many chemical pollutants, ashes, etc.). Waste containing chromates, amphoteric metals such as Pb and Zn, and waste with some soluble salts content, need pretreatment before the immobilisation process. Some wastes not suitable for immobilisation include:

- flammable and highly flammable wastes (e.g. low flashpoint solvents)
- wastes containing volatile substances. Sometimes very low concentrations of VOCs may be accepted
- oxidising agents. Sometimes very low concentrations of oxidising agents may be accepted
- odorous wastes. Sometimes very low odour materials may be accepted
- waste containing highly soluble organic waste and a high COD content
- waste containing molybdenum
- waste containing soluble inorganic salts
- solid cyanides. Sometimes very low concentration of cyanides may be accepted
- chelating agents. Sometimes very low concentration of chelating agents es may be accepted.

Some of the wastes mentioned above may be treated by some specific reagents. For example, cement (as shown in Table 4.6) and lime reagents are compatible with oxidising agents.

#### **Economics**

Cold processes are considered economically attractive techniques. They typically require simple equipment and incur low investment (concrete mixers, silos, pumps, etc.) and operational costs.

Reagents/binders are used when possible to lower the treatment costs (fly ashes from power stations, slag from steel mills, the residues of cement furnaces). Operators are not always in a position (because of regulations, of availability in the surrounding, of interest in a specific waste, etc.) to use wastes as reagents, although it is of course generally economically viable.

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### **Driving force for implementation**

Landfill Directive 1999/31/CE. Simple physical dilution or absorption, which does not lead to any associated physico-chemical change, is not an acceptable treatment process. For example, the absorption of a liquid into sawdust, so that it is no longer a liquid waste, is not acceptable as a pretreatment for landfill.

### **Example plants**

13 plants stabilise around 400 kilotonnes of hazardous waste before landfilling, according to the French regulation and, from 2004 – 2005, to the EC regulation. Mobile units are also available to treat some waste spots on industrial sites.

In Portugal, one plant stabilise MSW incineration fly ashes before they are landfilled.

### **Reference literature**

[51, Inertec, et al., 2002], [52, Ecodeco, 2002], [53, LaGrega, et al., 1994], [55, UK EA, 2001], [136, Straetmans, 2003], [150, TWG, 2004]

## **4.2.4. Cement solidification**

### **Description**

Generally wastes are mixed with portland cement and additives to control the properties of the cement, and enough water to ensure that hydration reactions will take place to bind the cement. Both stabilisation and solidification processes take place. The wastes are thereby incorporated into the cement matrix. Typically, the waste IN will react with water and the cement to form, to some extent, metal hydroxides or carbonates which are usually less soluble than the original metal compounds in the waste matrix.

Cement-based solidification techniques rely on the use of equipment that is typically readily available. The mixing and handling associated with the processes are well developed and the technique is robust with respect to variations in waste IN characteristics.

The solidified product is either landfilled in surface level or underground deposits. In some countries, it may be utilised as a backfilling material in old salt mines.

### **Achieved environmental benefits**

The main advantage of cement solidification is the reduced contact between water and waste IN and to some extent the formation of less soluble metal hydroxides or carbonates. Amphoteric metals can also be treated. The solidified product is relatively easy to handle, and the risk of dust formation is very low. The release of heavy metals from the products in the short term is typically relatively low. The technique does, in some cases, facilitate utilisation of the waste OUT as backfilling or construction material in the mining industry.

Recent developments in this technology have been undertaken by incorporating additives to bind difficult contaminants before encapsulation. Difficult contaminants are considered to be arsenic, lead, phenols (including PCP), PCBs and dioxins. There is evidence that cement can catalyse or participate in the reductive dechlorination of TCE.

### **Cross-media effects**

Most studies have focused on the possible short term releases of contaminants from the waste OUT. The long term behaviour of the waste OUT is much less understood. It must be expected that the leaching of lime over time will change the chemical properties of the waste OUT, and also that increased leaching may occur as the pH decreases. The time required for a complete release from stabilised waste OUT can, however, be expected to be in the range of several hundred to a thousand years. The high pH level of cement-based systems can result in a significant leaching of amphoteric metals (Pb and Zn).

The drawbacks of this method are that leaching of soluble salts is not hampered and that this can eventually result in physical disintegration of the solidified product, thus allowing further leaching. In this case, the entry of air may result in some carbonation, partially rectifying the increase in porosity and loss of strength.

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The addition of cement and additives increases the amount of waste to be handled; typically about 30 – 50 % of the waste IN dry weight is added as cement and additives, and 30 to 100 % of the total dry weight is added as water. Thus, the waste OUT is typically increased from 20 - 30 kg/tonne waste input to about 40 – 60 kg/tonne waste, including an addition of water corresponding to 50 % of the total dry weight.

If the heavy metals are not recovered from the residues, which is potentially possible but a costly and energy consuming process, the contaminants will sooner or later be released. It should be emphasised that these time perspectives mean that the dominant part of the metals in questions will be released at a time when all leachate collection activities from the landfills will probably have been discontinued for many years. In addition, the location of the deposit may have been forgotten, as the area in question will most probably have by then been used for other purposes for a long time.

Cement may contain some toxic components such as pulverised fuel ash, cement kiln dust, blast furnace slag and bitumen.

#### **Operational data**

Energy and water consumption varies and is not quantified. The operation and control of equipment used by the technique is considered relatively simple and comparable with standard practices in the concrete industry.

#### **Applicability**

Solidification is typically performed at dedicated plants located near the end-destination of the final material; thus individual incinerators have no need to install solidification equipment. The technique can be used on all types of FGT wastes. Solidification with cement has also been used on many other types of hazardous wastes, including for the disposal of low level radioactive waste. More information on the applicability of the cement technique can be found in Table 4.6 in the next Section 4.2.5.

#### **Economics**

In most cases the waste IN can be delivered to existing plants. Treatment costs for cement solidification alone is estimated to about EUR 25 per tonne waste IN.

#### **Driving force for implementation**

The technique is relatively simple to use and the necessary technical knowledge is widely available. The leaching characteristics of the solidified product can be improved considerably compared to the untreated waste IN. Stabilisation of FGT wastes by cement solidification has long been, and is still considered, acceptable by authorities in many countries worldwide. The main reason for implementing this technology in Holland has been lack of hazardous waste landfill capacity.

#### **Example plants**

The technique is probably the most commonly used method for the treatment of FGT wastes and is widely used in Europe and Japan. Some examples of cement solidification are listed below:

Country	Characteristics
Austria	A plant for cement solidification for slag and ashes from MSW incineration is in operation in Vienna
Germany	Several salt mining companies accept several types of wastes (e.g. FGT waste, slags, demolition material from buildings) and perform cement solidification on these by using residues as filler material. The solidified wastes OUT are chiefly utilised as backfilling material or for reinforcement. Cement solidification is for some mines performed at one central plant using varying recipes according to

	final destination and requests. From the central solidification plant, the product is transported to the recipient mine
Sweden	At one landfill site in Sweden (Hogdalan) cement solidified FGT waste are cast into blocks and placed at a surface level landfill after hardening
Switzerland	A variation of cement solidification is used in Switzerland (initially funded by the Swiss government and Sulzer) where waste IN are washed with water at liquid solid ratio of 2:1 and dewatered prior to mixing with cement. This has the benefit of removing most of the soluble salts from the waste IN, thus improving the longevity of the solidified product. After solidification, the waste OUT is deposited at surface level landfills before hardening. In some plants, the mixture is cast into moulds to produce blocks, that are then transported to surface landfills

**Table 4.5: Cement solidification examples**  
[124, Iswa, 2003], [150, TWG, 2004]

#### Reference literature

[113, COWI A/S, 2002], [124, Iswa, 2003], [150, TWG, 2004], [152, TWG, 2004]

### 4.2.5. Use of other reagents in the immobilisation process

#### Description

Some techniques are:

- encapsulation by bitumen
- carbonisation using CO<sub>2</sub>
- immobilisation with clay minerals.

#### Achieved environmental benefits

Fly ash particles can be encapsulated by bitumen, and potential contact with water is thus restricted. This improves the leaching properties of the fly ash; probably allowing less heavy metals to be released than in the case of cement solidification.

Waste incineration residues may be stabilised by carbonation (using CO<sub>2</sub>), rather than hydration (with or without cement addition). Carbonation has a dramatic influence on the leaching of Pb and Zn and results in a lower pH product (around 9) but without loss of acid neutralisation capacity.

#### Cross-media effects

On bitumen encapsulation, no information on the possible leaching of dioxins from the solidified ash particles has been found, but it is noted that the solidification method itself does not reduce the original content.

#### Applicability

Waste component	Cement-based reagent	Pozzolan-based reagent	Thermoplastic reagent	Organic polymer reagent
Nonpolar organics	May impede	May impede setting.	Organics may	May impede

Waste component	Cement-based reagent	Pozzolan-based reagent	Thermoplastic reagent	Organic polymer reagent
such as: <ul style="list-style-type: none"> <li>oil and grease</li> <li>aromatic hydrocarbons</li> <li>halogenated hydrocarbons</li> <li>PCBs</li> </ul>	setting. Decreased durability over a long time period. Volatiles may escape upon mixing. Demonstrated effectiveness under certain conditions	Decreased durability over a long time period. Volatiles may escape upon mixing. Demonstrated effectiveness under certain conditions	vaporise upon heating. Demonstrated effectiveness under certain conditions	setting. Demonstrated effectiveness under certain conditions
Polar organics such as: <ul style="list-style-type: none"> <li>alcohols</li> <li>phenols</li> <li>organic acids</li> <li>glycols</li> </ul>	Phenol will significantly retard setting and will decrease the durability in the short run and over a long time period	Phenol will significantly retard setting and will decrease the durability in the short and over the long run. Alcohols may retard setting.	Organics may vaporise upon heating	No significant effect on setting
Acids: <ul style="list-style-type: none"> <li>hydrochloric acid</li> <li>hydrofluoric acid</li> </ul>	No significant effect on setting. Cement will neutralise acids. Types II and IV portland cement give better durability characteristics than Type I. Demonstrated effectiveness	No significant effect on setting. Compatible, will neutralise acids. Demonstrated effectiveness	Can be neutralised before incorporation	Can be neutralised before incorporation. Urea formaldehyde demonstrated to be effective
Oxidisers such as: <ul style="list-style-type: none"> <li>sodium hypochlorate</li> <li>potassium permanganate</li> <li>nitric acid</li> <li>potassium dichromate</li> </ul>	Compatible	Compatible	May cause matrix breakdown. Fire risk	May cause matrix breakdown. Fire risk
Salts such as: <ul style="list-style-type: none"> <li>sulphates</li> <li>halides</li> <li>nitrites</li> <li>cyanides</li> </ul>	Increased setting times. Decreased durability. Sulphates may retard setting and cause spalling unless special cement is used. Sulphates accelerate other reactions	Halides are easily leached and retard setting. Sulphates can retard or accelerate reactions	Sulphates and halides may dehydrate and then rehydrate, causing splitting	Compatible
Heavy metals such as: <ul style="list-style-type: none"> <li>arsenic</li> <li>cadmium</li> <li>chromium</li> <li>lead</li> <li>mercury</li> </ul>	Compatible. Can increase setting time. Demonstrated effectiveness under certain conditions	Compatible. Demonstrated effectiveness on certain species (lead, cadmium, chromium)	Compatible. Demonstrated effectiveness on certain species (copper, arsenic,	Compatible. Demonstrated effectiveness with arsenic

Waste component	Cement-based reagent	Pozzolan-based reagent	Thermoplastic reagent	Organic polymer reagent
			chromium)	

**Table 4.6: Reagent applicability for waste stabilisation**  
[53, LaGrega, et al., 1994]

Bitumen encapsulation has been used on fly ash only and not for the residues from dry and semi-dry FGT systems, indicating that these may present problems.

#### Example plants

Solidification treatment by bitumen has been practised in the Netherlands, carbonisation of waste incineration residues have been practised in the UK and immobilisation by clay minerals in Austria.

#### Reference literature

[53, LaGrega, et al., 1994], [124, Iswa, 2003], [150, TWG, 2004],

### 4.2.6. Phosphate stabilisation

#### Description

Chemical stabilisation using phosphate as the stabilisation agent is used. The treatment process is relatively simple, and consists of a mixing device (such as a pugmill) into which the wastes IN are fed at a controlled rate. A proprietary form of soluble phosphate is then added to the mixer. After the phosphate is thoroughly mixed with the waste IN, a conveyor at the end of the mixer then removes the treated product. In some cases, depending on the characteristics of the waste IN, other additives such as lime are used. Reaction kinetics are fast and the material is considered fully treated without further curing. Sometimes phosphate addition is used together with carbonation in order to bind some metals in the waste (e.g. Pb).

#### Achieved environmental benefits

The process retains salts in the waste OUT. Compared to the other similar processes relatively small amounts of water are added along with the phosphate. The process produces no waste water.

#### Cross-media effects

There are currently no suggestions for utilisation of the treated product. A substantial leaching is possible after landfilling as is the case with some heavy metals due to increased solubility (e.g. Cd). The release of salt and heavy metals in the landfill is expected to be higher than is the case with other treatments. Phosphate stabilisation may enhance phosphorus compound mobility of deposited waste. In one case, it has been shown that the total phosphate availability has increased from 2 mg/kg (before treatment) to 4900 mg/kg (after treatment).

#### Operational data

The specific amounts of water and phosphate, as well as other additives, are likely to vary according to the properties of the waste IN, however no quantification of this has been made available.

#### Applicability

The process is in all but one case implemented as an integrated unit at the incinerator, but it could also be set up to act as a centralised plant treating residues from more than one incinerator. The process was originally developed to treat MSW incinerator residues, however several other waste types (e.g. contaminated soil, slags, sludges, etc.) have been tried and tested.

#### Economics

The treatment cost is about EUR 15 per tonne of FGT waste. In addition to this, a royalty is charged for the use of the patented process amounting to EUR 5 – 10 per tonne. Investment costs are in the order of about EUR 150000 – 500000 per installation depending on existing equipment.



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### **Driving force for implementation**

The main reason for implementation of this technique is its simplicity of operation. Currently, it finds extensive commercial use in the United States, Japan and Taiwan. The treated product is generally accepted as suitable for landfilling in these countries.

### **Example plants**

The process is currently used in the United States, Japan and Taiwan at about 90 MSW incinerator facilities, treating over 2 million tonnes of bottom ash and FGT waste per year.

### **Reference literature**

[124, Iswa, 2003], [150, TWG, 2004], [152, TWG, 2004]

## **4.2.7. Thermal treatments of solid waste**

### **Description**

These techniques includes vitrification, melting and fusion of solid wastes (see Section 2.3.2). Its application to solid waste from waste incinerators is covered in the WI BREF.

### **Achieved environmental benefits**

Several techniques can be used for heating the solid wastes: electrical melting systems, fuel fired burner systems or blast melting. These differ only in the way the energy is transferred to the solid material. Generally techniques are inspired from furnaces used in iron and steel production.

Depending on the melting system, metal alloys may be recovered from the reaction chamber. Depending on the temperatures in the reaction chamber and the state of oxidation or reduction of the gas phase, heavy metals (especially Cd and Pb) may be volatilised and removed with the off-gas. All process configurations need off-gas treatment systems to minimise emissions.

An inherent advantage of these processes is the resulting destruction of organic pollutants, i.e. dioxins. Thermal treatment facilities in general reduce the volume to about 30 – 50 % of the input volume. Melting increases the density of the products to typically 2.4 – 2.9 tonnes/m<sup>3</sup>.

Melted and vitrified products generally have very good retention properties, but Swiss studies show that sintered products also reach about the same level of stability with regard to retention. Vitrification typically yields the most stable and dense products.

### **Cross-media effects**

A major drawback to these techniques is that they require substantial amounts of energy input.

Vitrification and melting result in a mobilisation of volatile elements such as Hg, Pb and Zn during the treatment process, which in some processes is used in combination with other parameters to produce a recyclable product low in heavy metals. Due to the release of vaporised heavy metals from the process, thermal treatment requires the additional of a flue-gas treatment system.

Thermal treatment processes use substantial amounts of energy. Additionally, the processes produce solid residues from the off-gas treatment. On the other hand, metals can be recovered from the process and, in some cases, even the vitrified product can be recycled.

### **Operational data**

Typically in the order of about 700 – 1200 kWh energy is used per tonne of treated material to reach and maintain the elevated temperatures, although figures of up to about 8000 kWh/tonne have been reported. Energy consumption and operation varies with the furnace type and plant design.

### Applicability

Usually, the waste IN should comply with certain requirements, for example: water content <5 %, unburned contents <3 %, metal content <20 % by weight, and ash size <100 mm.

Thermal treatment is used for the treatment of bottom ashes, as well as for combinations of bottom ash and FGT waste. Due to the typically high contents of salts and heavy metals in the FGT waste, the separate treatment of FGT waste may necessitate a requirement for extensive off-gas treatment, thus reducing the overall benefits of separately treating these materials.

### Economics

The technique is typically rather expensive compared to other treatment options. Treatment costs are reported to be in the order of EUR 100 – 500/tonne of input. Investment costs could be about EUR 20 million for a plant with a capacity to deal with 1 – 1.5 tonne/hour.

### Driving force for implementation

The main reason for implementing the technique is the good retention properties of the final product; especially in the case of vitrifying, and the significant reduction in volume. In densely populated areas, such as Japan, landfill capacity can be a scarce resource and landfilling can thus be relatively costly. Organic compounds such as dioxins and furans are almost completely destroyed.

### Example plants

There are 30 – 40 melting and vitrification plants in Japan and there are also plants operating in Europe and the US.

Country	Characteristics		
US	A vitrification process includes initial steps such as water extraction, dewatering and drying at 500 °C before the addition of glass forming additives and melting. The initial washing and drying is carried out to remove chlorides and residual organic carbon		
Japan	Plants for the thermal treatment of both bottom ash and FGT waste:		
		In operation	Planned Capacity (tonne/day)
	<i>Electric melting:</i>		
	Electric arc	4	2 655
	Plasma arc	4	2 183
	Electric resistance	2	3 148
	<i>Burner:</i>		
	Reflecting surface	12	209
	Rotating surface	5	84
	<i>Blast melting:</i>		
	Coke bed	3	170
	Residual carbon combustion	1	15
	Total	31	7 1464

Table 4.7: Thermal treatment plants  
[124, Iswa, 2003]

### Reference literature

[124, Iswa, 2003], [150, TWG, 2004]

## 4.2.8. Recovery of salts by solution/evaporation

### Description

When solid wastes are produced, the recovery potential can be considered. The recovery of, e.g. salts (NaCl, CaCl<sub>2</sub>, HCl and gypsum) may be a possibility. These products could be obtained by evaporation or recrystallisation of the salt from the flue-gas cleaning system of waste water, either locally or at a centralised evaporation plant.

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When the scrubber fluid is treated separately and subjected to evaporation, recoverable products like salts or hydrochloric acid can be obtained. The reutilisation potential of such products strongly depends on the product quality. In salt recovery, the scrubber liquid is treated with sodium hydroxide and calcium carbonate to produce solid gypsum, which after separation leaves a liquid containing mainly sodium and calcium chloride. The recovered products are subjected to quality control or even treated further for quality improvement and then traded off.

#### **Achieved environmental benefits**

The main objective of the operation is to avoid the discharge of saline waste water to the sewerage system. This is achieved by evaporation of the scrubber liquid from the wet flue-gas treatment system.

If solid sodium chloride needs to be separated individually from the above solution this is achieved by evaporation of the solution to a salt content of more than 30 %, at which level pure salt is crystallised. The above recovered salt products are most commonly reutilised in areas with a de-icing demand in winter time.

The re-use of the recovered salts and gypsum may save natural resources.

#### **Cross-media effects**

The major drawbacks of external waste water evaporation for salts not only related to operational and material problems but also to the high energy consumption necessary for evaporation.

#### **Operational data**

The evaporation of waste water containing salt is dependent on the salt concentration, which can vary greatly. Apart from problems of corrosion, the relatively high investment and operational costs need to be taken into account.

For the production of gypsum only a few operational problems exist. However, the gypsum quality is determined not only its purity with respect to the presence of other undesirable components but also due to its colour. Normally, a production of recyclable products of about 2 - 5 kg/tonne of waste can be expected.

By producing calcium chloride, focus should be put on the extreme corrosion potential that may arise and risk an unintended phase shift from a solid to a liquid state and vice versa.

#### **Applicability**

Can be applied in municipal waste incinerators with wet flue-gas treatment systems. For MSW incinerators with wet scrubbing of the incineration flue-gas, no discharge of the waste water is permitted due to legislation and local demands. The cleaned waste water from the wet scrubbers will still contain salts that are normally not desirable in the sewage pipe system because can cause corrosion or increase the salt content of fresh water bodies. For this reason the waste water is normally treated thermally and, where the waste water is used for cooling, by injection to and evaporation in the raw incinerator flue-gas. Here, no recoverable products are obtained.

Evaporation of treated saline waste water can be done at both centralised and decentralised plants. In the latter case, the MSW incinerator itself could supply the energy needed for evaporation.

For gypsum production, this could be achieved primarily operational changes only, i.e. implementation and operation of suitable dewatering devices, including cyclones, pumps, etc.

#### **Economics**

The costs for evaporation and storage of the recovered products are several times the costs for production of the same salts from natural resources. Thus, this technique is primarily applied for environmental reasons rather than for economic reasons.

Due to the production of already large amounts of high quality gypsum from energy production processes at power plants, gypsum produced in the above manner from MSW incinerators is only used for applications with a lower demand of gypsum quality. If re-use is not possible, then the gypsum has to be disposed of, thus incurring a corresponding disposal cost.

### Driving force for implementation

Due to legislation, the discharge of scrubber liquid from wet flue-gas systems should be minimised. Even though the waste water is intensively treated for removal of, e.g. heavy metals and other harmful impurities, this hardly affects the total amount of salts. A substantial reduction of salt emission from the individual MSW incinerator to the local surrounding area is only accomplished by evaporation of the scrubber liquid. By separation of the solid gypsum, the amount of FGT waste for disposal is reduced.

### Example plants

Evaporative processes have been implemented with success in several countries, especially in Germany where several incineration plants have applied this technology.

### Reference literature

[124, Iswa, 2003], [150, TWG, 2004], [152, TWG, 2004]

## 4.2.9. Acid extraction

### Description

A number of techniques use acid extraction; some examples are given in Table 4.8:

Process	Characteristics
Acid extraction process	This process combines an acid extraction of soluble heavy metals and salts by using the (acidic) scrubber blowdown. Before using the scrubber liquid, mercury is removed by either a filtration (when activated carbon is introduced into the scrubber) and/or a specific ion exchanger. Both boiler ash and fly ash are treated this way. The L/S ratio in the extraction step is about 4; pH is controlled at 3.5 by the addition of hydrated lime. Within the residence time of about 45 minutes, sulphate (from the SO <sub>2</sub> scrubber) is precipitated to gypsum. The solid residue is dewatered, then countercurrently washed on a belt filter and finally landfilled, normally as a mixture with bottom ash. The filtrate has to be treated in order to remove heavy metals by neutralisation, precipitation and ion exchange. The dewatered and rinsed filter cake contains about 25 % zinc and is therefore recycled in metallurgical processes
Combination of acid extraction with thermal treatment	This process combines acid extraction with thermal treatment. First, boiler and fly ash are washed with the first stage wet scrubber solution, and dewatered. Then the solid residues are treated in a rotary kiln for one hour at around 600 °C destroying majority of the organic compounds and volatilising Hg. The off-gas is treated in an activated coal filter. The waste water is treated to remove heavy metals. The scrubber solution from the second scrubber is used to wash the bottom ash and to neutralise acidic effluent streams
Acid extraction sulphide process	This process combines fly ash and NaOH scrubber solution with water with an L/S ratio of 5. After mixing, the pH is adjusted to about 6 – 8 with HCl to extract heavy metals, and NaHS is added to bind heavy metals as sulphides. Then a coagulation agent is added and the slurry is dewatered. The filter cake is landfilled, and the waste water is treated in a subsequent treatment unit to remove heavy metals

**Table 4.8: Acid extraction technologies**  
[124, Iswa, 2003], [150, TWG, 2004]

### Achieved environmental benefits

The process can remove a significant part of the total amount of heavy metals from the waste IN (Cd: ≥85 %; Zn: ≥85 %; Pb and Cu: ≥33 %; Hg: ≥95 %); the leachability of the material is reduced by a factor 10<sup>2</sup> – 10<sup>3</sup>. Zinc, cadmium and mercury are recycled.

### Cross-media effects

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The dioxin content of the bottom ash increases when the treated ash is disposed of 'as combined' with bottom ash; however, the leaching potential of the mixture is higher because of the higher density.

#### **Operational data**

Most of the plants that operate for 24 hours can adapt the weekly operation period (4 – 7 days) according to the arising FGT waste.

#### **Applicability**

The system can be used only on incinerators with a wet FGT system having a permit allowing a discharge of treated waste water.

#### **Economics**

The process costs of treating the FGT waste are about EUR 150 – 250/t (including charges for recycling the zinc filter cake).

#### **Driving force for implementation**

This technique provides a method to treat solid waste according to Swiss legislation at competitive (compared to the export for German underground disposal) costs.

#### **Example plants**

Start-up of the first plant was in 1996. Six plants currently operate in Switzerland and one in the Czech Republic.

#### **Reference literature**

[124, Iswa, 2003], [152, TWG, 2004]

### **4.2.10. Excavation and removal of contaminated soil**

#### **Description**

Some techniques include:

- a. identifying and operating ways to reduce fugitive emissions by proper management of the site
- b. enclosing the remediation within a dome and applying treatment to the air
- c. controlling the rate of excavation, the amount of contaminated soil area that is exposed, and the duration that soil piles are left uncovered. The timing of excavation can also be important. Scheduling excavation during times of the day or seasons of the year when wind speeds and temperatures are low can reduce emissions. The work can also be scheduled to avoid seasons with dry soil conditions to further minimise emissions.

#### **Achieved environmental benefits**

Reduces the fugitive emissions generated by the excavation and removal of contaminated soil. VOC emission control also can be achieved by controlling the operating conditions within preset parameters.

#### **Cross-media effects**

Some releases of volatile contaminants are inevitable during excavation. Stagnant wind conditions may lead to unacceptable ambient air concentrations at the work site.

#### **Applicability**

Enclosure of the remediation within a dome is not a commonly use measure.

#### **Reference literature**

[30, Eklund, et al., 1997]

### **4.2.11. Thermal desorption of soil**

#### **Description**

See Section 2.3.9. Some techniques include:

- 
- a. using of a bench-scale test to determine the suitability of thermal desorption and the best residence time and temperature to use. The effectiveness of thermal desorption is related to the final soil temperature that is achieved, which in turn is a function of residence time and heat transfer. The temperatures and residence times effective in bench-scale systems also have proven to be effective in pilot scale systems
  - b. applying the appropriate temperature. The typical treatment temperature range for petroleum fuels from leaking underground storage tank sites is 200 to 480 °C. For the treatment of soils containing pesticides, dioxins, and PCBs, temperatures need to exceed 450 °C
  - c. reducing the moisture content of the soil to be treated within a specified range, this being applied due to the cost of treating waste with a high water content. The typical acceptable moisture range for rotary dryers and asphalt kilns is 10 – 30 %, while thermal screw systems can accommodate higher water loadings of 30 – 80 %. To remove VOCs, the soils should ideally contain 10 – 15 % moisture as the water vapour can carry out some of the VOCs
  - d. having in place collection and control equipment such as afterburners, thermal oxidisers, fabric filters, activated carbon, or condensers for the treatment of gases.

#### **Achieved environmental benefits**

Flexibility, as thermal desorption can treat a wide range of organic contaminants and the systems can be mobile. Thermal desorbers operate at lower temperatures, so significant fuel savings may result when compared to incineration. They also produce smaller volumes of off-gases to be treated. Typical specifications for thermal desorption systems are shown in Table 4.9.

	Rotary dryer	Asphalt plant	Thermal screw	Conveyor furnace
Mobility	Fixed and mobile	Fixed	Mobile	Mobile
Typical site size (tonnes)	450 – 23000	0 – 9000	450 – 4500	450 – 5000
Soil throughput (tonnes/hour)	9 – 45	23 – 90	3 – 14	5 – 9
Maximum soil feed size (cm)	5 – 8	5 – 8	3 – 5	3 – 5
Heat transfer method	Direct	Direct	Indirect	Direct
Soil mixing method	Shell rotation and lifters	Shell rotation and lifters	Auger	Soil agitators
Discharge soil temperature (°C)	150 – 300 <sup>a</sup> 300 – 650 <sup>b</sup>	300 – 600	150 – 250 <sup>c</sup> 300 – 250 <sup>d</sup> 500 – 850 <sup>e</sup>	300 – 800
Soil residence time (minutes)	3 – 7	3 – 7	30 – 70	3 – 10
Thermal desorber exhaust gas temperature (°C)	250 – 450 <sup>a</sup> 400 – 500 <sup>b</sup>	250 – 450	150	500 – 650
Gas/solids flow	Co-current or countercurrent	Co-current or countercurrent	Not applicable	Countercurrent
Atmosphere	Oxidative	Oxidative	Inert	Oxidative
Afterburner temperature (°C)	750 – 1000	750 – 1000 <sup>f</sup>	Generally not used	750 – 1000
Maximum thermal duty (MJ/hr <sup>g</sup> )	10500 – 105000	5300 – 105000	7400 – 10500	10500
Heatup time from cold condition (hours)	0.5 – 1.0	0.5 – 1.0	Not reported	0.5 – 1.0
Cool downtime from hot condition (hours)	1.0 – 2.0	1.0 – 2.0	Not reported	Not reported
Total petroleum hydrocarbons				
Initial concentration (mg/kg)	800 – 35000	500 – 25000 <sup>h</sup>	60 – 50000	5000
Final concentration (mg/kg)	<10 – 300	<20 <sup>h</sup>	ND – 5500	<10.0
Removal efficiency (%)	95.0 – 99.9	Not reported	64 – 99	>99.9
BTEX				
Initial concentration (mg/kg)	Not reported	Not reported	155	Not reported
Final concentration (mg/kg)	<1.0	Not reported	<1.0	<0.01
Removal efficiency (%)	Not reported	Not reported	>99	Not reported
<sup>a</sup> Carbon steel materials of construction <sup>b</sup> Alloy materials of construction <sup>c</sup> Hot oil heat transfer system <sup>d</sup> Molten salt heat transfer system <sup>e</sup> Electrically heated system <sup>f</sup> Not used on all systems <sup>g</sup> Total duty of thermal desorber plus afterburner <sup>h</sup> Vendor information				

**Table 4.9: Comparison of features of thermal desorption and off-gas treatment systems [30, Eklund, et al., 1997]**

### Cross-media effects

In order to destroy contaminants, the desorption process needs a subsequent afterburning and waste gas treatment. The reason is that desorption merely strips them from the solid or liquid phase and transfers them to the gas phase. Therefore, devices to control air emissions are necessary. The efficiency of the thermal desorption process will vary with the chemical and physical properties of the specific contaminants. Metals (e.g. lead) tend to remain in the soil after treatment, so additional soil processing or treatment may be required (e.g. stabilisation). Thermal desorbers may operate near or above 500 °C, so some pyrolysis and oxidation may occur, in addition to the vaporisation of water and organic compounds.

### Applicability

Applicable to soils contaminated with volatile compounds at the operating temperature. High molecular weight organic compounds may foul or plug baghouses or condenser systems. Therefore, the types of petroleum

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products that can be treated by specific technologies may be limited. Rotary dryers can typically treat soils that have an organic content of less than 2 %. Thermal screw units may treat soils that contain up to 50 % organics.

**Economics**

Typically cheaper than incineration.

**Driving force for implementation**

Thermal desorption differs from incineration with regard to the regulatory and permitting requirements. Perhaps most importantly, thermal desorption enjoys more public acceptance than other thermal treatment methods.

**Reference literature**

[30, Eklund, et al., 1997], [51, Inertec, et al., 2002], [150, TWG, 2004]

## **4.2.12. Vapour extraction**

**Description**

See Section 2.3.10. As the vapours are removed from the solid waste, they are treated to reduce air emissions. Direct combustion is theoretically possible if the hydrocarbon content of the exhaust gas is high enough, but the concentration typically drops significantly during removal. Therefore, natural gas or some other fuel would be needed to maintain combustion. Also, for safety reasons, dilution air is typically added to maintain the VOC concentration below the lower explosive limit. For lower levels of hydrocarbons, catalytic oxidation or carbon adsorption may be effective.

**Achieved environmental benefits**

Air emissions are released from a point source and, thus, can readily be controlled. The success of the method varies with the volatility (vapour pressure) of the contaminants present.

**Cross-media effects**

Significant residual contamination may remain in the solid waste after treatment.

**Operational data**

The equipment is simple to install and operate.

**Applicability**

The treatment is applicable to excavated soil. However, it is not applicable for saturated soils or for soils with low air permeabilities, but it is applicable to the treatment of soil contaminated with PCBs.

**Economics**

Large volumes of excavated soil can be treated in a cost-effective manner.

**Reference literature**

[30, Eklund, et al., 1997], [100, UNEP, 2000], [150, TWG, 2004], [152, TWG, 2004]

## **4.2.13. Soil washing**

**Description**

See Section 2.3.13. Some techniques include:

- a. recycling the blowdown water as much as possible
- b. using carbon filters for the treatment of collected air emissions from the waste site or soil washing unit
- c. ensuring that the sludge and solids from waste water treatment are subjected to appropriate treatment and disposal.

**Achieved environmental benefits**



Installation	Contaminants	Concentration in the untreated soil (ppm)	Range of removal efficiencies (%)	Residual concentrations (ppm)
1	Oil and grease		50 – 83	250 – 600
2	Pentachlorophenol		90 – 95	<115
	Other organics		85 – 95	<1
3	Oil and grease		90 – 99	<5 – 2400
4	Volatile organics		98 – >99	<50
	Semi-volatile organics		98 – >99	<250
	Most fuel products		98 – >99	<2200
5	Aromatics		>81	>45
	Crude oil		97	2300
6	Total organics		96	159 – 201
	PAHs		86 – 90	91.4 – 97.5
7	Oil		>99	20
8	Hydrocarbons		96.3	82.05
	Chlorinated hydrocarbons		>75	<0.01
	Aromatics		99.8	<0.02
	PAHs		95.4	15.48
9	Fuel oil	7666	65	2650
10	Fuel oil	7567	73	2033
11	Fuel oil	9933	72	2833

**Table 4.10: Summary of the performance data for soil washing [30, Eklund, et al., 1997]**

Table 4.10 below presents some indicative general efficiencies for soil washing treatment.

Pollutants	General Efficiency <sup>1</sup>
TPH (C <sub>10</sub> -C <sub>40</sub> )	90 – 98
PAHs	90 – 97
BTEX	90 – 97
PCBs	90 – 97
Metals	
As	60 – 80
Cd	60 – 80
Cr	80 – 90
Cu	75 – 85
Hg	85 – 95
Ni	85 – 90
Pb	90 – 95
Zn	85 – 95
<sup>1</sup> General Efficiency = (1 - conc in decontaminated sand/conc in polluted soil) * 100	

**Table 4.11: Efficiencies of different components for soil washing [123, Perseo, 2003]**

#### Reference literature

[30, Eklund, et al., 1997], [123, Perseo, 2003]

#### 4.2.14. Solvent extraction

##### Description

See Section 2.3.11.

##### Achieved environmental benefits

Compound	Initial concentration (mg/kg)	Final concentration (mg/kg)	Removal (%)
Anthracene	28.3	0.12	99
Benzene	30.2	0.18	99
Benzo(a)pyrene	1.9	0.33	83
Bis-(2-ethylhexyl)phthalate	4.1	1.04	75
Chrysene	6.3	0.69	89
Ethylbenzene	30.4	0.23	99
Naphthalene	42.2	0.66	98
Phenanthrene	28.6	1.01	96
Pyrene	7.7	1.08	86
Toluene	16.6	0.18	99
Total xylenes	13.2	0.98	93

**Table 4.12: Results of the remediation of API separator sludge by solvent extraction**  
[30, Eklund, et al., 1997]

##### Applicability

Applicable for the removal of PCB from soil. The contaminated solvent must then be treated to destroy the PCBs.

##### Reference literature

[30, Eklund, et al., 1997], [100, UNEP, 2000]

#### 4.2.15. Evaporation

##### Description

Evaporation is typically an important part of the Ph-c treatment facility. The evaporation treatment facility concentrates the hazardous waste. The concentrate is typically burned. The sewage (condensate) is stored temporarily and after analysis and control, it will be transported to a waste water treatment plant. The exhaust air will be cleaned with a carbon filter.

Before evaporation certain pretreatments are carried out in the Ph-c treatment facility. These are flocculation, precipitation, ultrafiltration and organic splitting. After evaporation, flocculation is carried out to the condensate if it is contaminated with oil. The exhaust air is treated by alkali launderer and carbon filter.

##### Achieved environmental benefits

Reduce the amount of waste water produced. The achievable levels in the exhaust air and in the waste water is shown in the Table 4.12 below.

Compound	Value	Unit	Charge	Unit
<i>Parameters of the exhaust air</i>				
TOC	63	mg/Nm <sup>3</sup>	96	kg/yr
<i>Parameters of the waste water produced</i>				
Temperature	30	°C		
pH-value	9.3			
Conductivity	900	µS/cm		
sedimentary substances (105 °C)	0.1	mg/l	2	kg/yr
BOD	3000	mg/l	60000	kg/yr
COD	5000	mg/l	100000	kg/yr
Hydrocarbons	2	mg/l	40	kg/yr
Phenol		mg/l		kg/yr
AOX	0.1	mg/l	2	kg/yr
Nitrite	0.01	mg/l	0.2	kg/yr
Cyanide	0.02	mg/l	0.4	kg/yr
Al	2	mg/l	40	kg/yr
Fe	0.1	mg/l	2	kg/yr
As	0.01	mg/l	0.2	kg/yr
Cr total	0.1	mg/l	2	kg/yr
Cr(VI)	0.01	mg/l	0.2	kg/yr
Cu	0.1	mg/l	2	kg/yr
Hg	0.001	mg/l	0.02	kg/yr
Ni	0.1	mg/l	2	kg/yr
Pb	0.1	mg/l	2	kg/yr
Zn	0.1	mg/l	2	kg/yr
Treated waste: 20000 tonnes per year				

**Table 4.13: Achievable levels of evaporation process carried out to waste waters**  
[147, UBA, 2003]

**Reference literature**  
[147, UBA, 2003]

#### 4.2.16. Purification and recycling of FGT wastes

##### Description

The sodium-based FGT wastes are mainly constituted of sodium chloride (as a result of HCl neutralisation), sodium sulphate (as a result of SO<sub>2</sub> neutralisation), sodium carbonate (result of sodium bicarbonate excess), fly ash and adsorbent (activated carbon or lignite coke).

In flue-gas single filtration systems, fly ash is mixed with neutralisation salts and the soluble part represents about 50 % of waste IN; in flue-gas double filtration systems, the first filter catches most of the fly ash and sodium-based FGT wastes collected at the second filter contain about 90 % soluble salts.

The process includes the following steps:

- mixing the FGT waste with hydraulic binders: prepares the solidification of the insoluble part
- dissolving in water and adding additives: the soluble part is dissolved and most heavy metals are precipitated

- 
- c. filtering this suspension: resulting products are a self-solidifying filter cake with a very low soluble fraction (after washing), and a raw brine containing soluble salts
  - d. purifying the brine (with various steps including ion exchange resins) in such a way that it may be re-used in the manufacture of sodium carbonate (soda ash).

This process has no outputs other than the solidified filter cake (to be landfilled) and the purified brine, which replaces part of the fresh raw material used by the soda ash plant: there is no liquid effluent at all.

#### **Achieved environmental benefits**

The technology described here realises the separation between soluble and insoluble parts of the FGT waste, solidifying the insoluble part and purifying and re-using the soluble part (constituted of inorganic salts) in some industries. Therefore:

- the landfilled solid part of FGT waste has a very low soluble fraction and so its solidification is better; so there is a lower consumption of hydraulic binders and a lower quantity of ultimate waste
- the soluble part of FGT waste is re-used in the chemical industry, replacing the use of fresh materials (salt is one of the main raw materials for soda ash plants). This soluble part is recycled at a rate higher than 95 %.

The treatments do not generate liquid effluents (all liquids are re-used as process water to form the recycled brine) and no significant air emissions are reported (ambient temperature process).

#### **Cross-media effects**

Not identified.

#### **Operational data**

The process does not require high energy input: it works at ambient temperature.

#### **Applicability**

It is applied to the FGT waste coming from the dry sodium bicarbonate flue-gas cleaning process used in municipal solid waste incineration. This process is implemented in dedicated and centralised plants located close to the soda ash plant using the produced purified brine, and which receive FGT waste coming from various MSW incineration plants.

#### **Economics**

This process is to be compared with the solidification and landfilling of FGT waste. From this point of view, (1) the solidification is much eased by the separation of the soluble part, and (2) the quantity of ultimate residues is reduced, this process has been reported to be competitive in some countries. Operational costs are low and the investment cost of the treatment plant is the key factor. So this process must be implemented in centralised units serving numerous incineration plants.

#### **Driving force for implementation**

This process is favoured by the following observed evolutions:

- severe ruling on landfilling: when safe solidification required
- resistance to new landfilling site projects as there is a trend to landfill as little as possible
- trend to promote recycling.

#### **Example plants**

Two plants work industrially using this process or slight variations of it: one in Italy (Toscana), capacity 10 kt FGT waste/yr, and one in France (Lorraine), capacity 50 kt FGT waste/yr. Both supply purified brine as raw material to a soda ash plant.

#### **Reference literature**

[150, TWG, 2004], [152, TWG, 2004]

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### 4.3. Physico-chemical treatments of specific wastes

#### 4.3.1. Treatment of oils contaminated with PCB

##### Description

The process is the dehalogenation of oils contaminated with PCBs from electrical transformers. The process also allows the elimination of low boiling compounds and oxidation products, which are responsible for the low dielectric properties of contaminated oil. At the end of the process, a filtration process is carried out in order to eliminate the by-products of the reaction.

##### Achieved environmental benefits

The process produces an oil with dielectric characteristics that make it possible to be re-used for the same purpose, with a content of PCB of less than 1 ppm.

##### Applicability

Applied to oil transformers with PCB contents of between 25 – 2000 ppm. The process can be applied to:

- dehalogenation and recovery of bulking ex-transformers mineral oils contaminated with PCBs
- cleaning and recovery of operating transformers containing mineral oils contaminated with PCBs. This step is performed by means of recirculation of the dehalogenated mineral oil and it permits the extraction of the residual PCB absorbed in the different components of the transformers (e.g. paper and wood).

##### Economics

The concentration range mentioned in the above Applicability section, is the typical range where this technique is found to be economically viable. Technically this is not a problem when applied at higher concentrations but it has been found that there are other types of PCB treatment processes more economically viable.

##### Driving force for implementation

It exists mobile systems that can be applied to transformers in operation without the need to move them.

##### Example plants

One example is operational in Italy.

##### Reference literature

[52, Ecodeco, 2002], [150, TWG, 2004]

#### 4.3.2. Thermochemical conversion of waste asbestos

##### Description

Thermochemical conversion technology uses a combination of chemical treatment and heat to bring about a re-mineralisation of asbestos and other silicate materials. The re-mineralisation process accomplishes several goals including:

- conversion of asbestos minerals into non-asbestos minerals, without the need for melting
- destruction of organic compounds, through pyrolysis and/or oxidation
- immobilisation of metals and radionuclides.

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The process involves shredding and then mixing material containing asbestos with fluxing agents and heating the fluxed mixture. The presence of the fluxing agents at elevated temperatures (approximately 1200 °C) results in the rapid re-mineralisation of asbestos fibres, which are converted into non-asbestos minerals such as diopside, wollastonite, olivine and glass.

The processing equipment consists of four primary systems which are feed preparation, rotary hearth converter, off-gas treatment, and product removal.

Pyrolysis of the organic compounds takes place in the rotary hearth. The pyrolysis products are directed via an induced draft to a thermal oxidation unit that destroys any residual organic contamination that might be present in the off-gas. From the thermal oxidiser, the off-gases are cooled and scrubbed of any particulates and acid components that might be present. The presence of demineralising agents accelerates molecular diffusion in inorganic waste during heating, which destroys inorganic compounds such as asbestos and causes a simultaneous oxidation and molecular bonding of metals and radionuclides within the waste media. This results in the immobilisation of metals and radionuclides. The process also results in significant volume reduction of the waste. The amount of volume reduction is dependent upon the type of material being treated and can range from 10 % for soils to over 90 % for materials containing asbestos or primarily organic materials.

#### **Achieved environmental benefits**

The technology provides treatment effectiveness equivalent to that of vitrification without the requirement for melting the waste. In particular it:

- converts asbestos materials into inert material
- results in a significant volume reduction of the waste. The volume of the treated product can be significantly reduced from the original waste (up to 90 %), but may ultimately require landfill disposal depending on the contaminants present.

The process also results in the destruction of organics, including PCBs to 99.9999 % destruction removal efficiency. Toxic metals are stabilised in the sintered product through molecular bonding and the technology developer believes that, based on preliminary testing, the process will also be effective for radionuclides.

#### **Applicability**

The process is also effective on other types of waste including demolition debris and predominantly organic waste. The technology is applicable to liquid and solid wastes that are reasonably homogeneous or that can be made so without excessive expense. The process can treat wastes contaminated with a variety of contaminants including organic contaminants such as VOCs; semi-volatile organic compounds; PCBs and dioxins; inorganic contaminants such as asbestos and cyanide; metals including arsenic, lead, chromium, barium, zinc, selenium, cadmium; radionuclides that can be vitrified such as transuranic elements, caesium, thorium and uranium; and mixtures of these contaminants.

Wastes for which there are limited data or for which it is believed that the technology is not economically viable or technically compatible include mercury, gaseous radionuclides such as <sup>14</sup>C, explosives and some chemical agents (although here it is believed that the technology may be applicable, but there are no data to support such a claim).

#### **Economics**

The technology provides treatment effectiveness equivalent to that of vitrification without the requirement for melting the waste. This makes the technology less expensive and more versatile than vitrification for certain wastes. The capital cost for the 37 tonnes per day unit is approximately USD 3 million. Using the assumptions presented at the end of this section, a 37 tonne/day system can treat material containing asbestos for approximately USD 175 – 225 per tonne.

The three largest most significant contributors to the overall cost are fuel, equipment, and labour. Fuel makes up approximately 36 % of the total cost, equipment makes up 30 %, and labour about 22 %. Other items such as reagents, maintenance, water, electricity, personal protection equipment and filters make up the remaining 12 % of the overall cost.

The cost estimates presented in this section are based on the following assumptions:

- system description: 37 tonne/day system, direct fired with heat recovery, with dry lime scrubber
- capital cost: based on a 7 year capital recovery period at a real discount rate of 3.0 % (2002)
- operating conditions: 24 h/day operation, 80 % operating efficiency, 9 person crew
- cost includes fuel (kerosene), electricity, process chemicals, personal protection equipment, regular maintenance, and HEPA filters
- overheads and profits are also included
- disposal of treated materials is not included
- transportation to the treatment facility is not included.

#### **Driving force for implementation**

Waste asbestos is typically disposed of in landfills. However, some of the asbestos can be contaminated with radionuclides, PCBs, metals. For this reason, those materials may require pretreatment prior to landfill disposal.

#### **Example plants**

A new plant is currently proposed in Ireland.

#### **Reference literature**

[94, USA DoE, 2002], [150, TWG, 2004]

### **4.3.3. Treatment of waste containing mercury**

#### **Description**

Some techniques are:

- pretreat the waste containing mercury as follows:
  - shredding/crushing of batteries and button cells
  - sorting/breaking/separating of thermometers and contactors
  - centrifuging the sludge containing mercury in order to remove most of the metallic mercury. The residual sludge has a low content of mercury and is treated in the vacuum distillation process
  - shredding/sieving the gas discharge lamps, removing the iron and separating it in fractions. The fluorescent powder containing mercury is treated in the vacuum distillation
  - end-cut/air-push treatment of the gas discharge lamps through heating and cooling the ends break. Afterwards, the fluorescent powder containing mercury is blown out (air-push). A selection unit can be added to this pretreatment technique. This detects the powders in order to selectively blow them out. Re-use of the powders is possible
- carry out the following sequence of treatments:
  - separate and concentrate the mercury by evaporation and condensation
  - treat the off gases with dust filters and activated carbon filters
  - return the dust and the contaminated carbon from the gas treatment into the process
- treat the distillate (water and organic fractions) by:
  - incineration in a waste incinerator
  - conducting the gases from the distillation through an after-burner (at approximately 850 °C) and a condenser. The off-gases are cleaned by flue-gas treatment (e.g. scrubber, dust filter and activated carbon filter). The separated dust and the contaminated carbon are returned to the distillation vessel. This alternative raises the recovery rate
  - purifying the water fraction (after separation) and returning the deposit to the distillation vessel. This alternative raises the recovery rate.

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### **Achieved environmental benefits**

The mercury is recycled as a secondary raw material. The destination of the residue from the vacuum vessel depends on the waste treated. It can be used as a secondary raw material (e.g. for batteries) or landfilled (e.g. in the case of sludge containing mercury).

In a thermal soil remediation plant, with a throughput of 2 t/h of soil containing mercury and with mercury raw gas concentrations of up to 20 mg/Nm<sup>3</sup>, a maximum removal rate of 99.9 % has been reported. It has also been reported that the mercury content of the soil (1 - 300 mg/kg) decreased to less than 5 mg/kg following thermal treatment. Another treatment reported a resulting percentage of the mercury emitted to the air as being 0.0015 %. The emissions range from 0.04 to 0.2 mg/Nm<sup>3</sup>.

In the vacuum distillation of the sludge containing mercury (1 – 4 % mercury), 99.6 % of the mercury is recovered. About 0.1 % of the mercury is left in the residue and about 0.15 % comes along with the distillate, which is to be incinerated. The latter percentage ends up in the off-gases. By means of the activated carbon filter, 99.9 % of this mercury is separated. The maximum concentration of mercury in the residue is 50 mg/kg DM.

### **Cross-media effects**

- consumption of energy for the distillation process and possible pretreatment
- consumption of activated carbon and water in the gas treatment
- emissions to air.

### **Operational data**

The consumption of electricity for the heating of the vacuum vessel and for the vacuum pump amounts to 3.5 GJ/t waste. The consumption of cooling water is approximately 13 t/t waste containing mercury. For the treatment of the sludge containing 2 % mercury, the activated carbon needed amounts to 24 kg/t sludge.

Because of the hazardous nature of the vapours containing mercury, safety measures are required. These include exhaust systems; test measuring; locks; safety procedures for filling, emptying and (dis)connecting the vacuum vessels; and decontamination facilities. To minimise the risk of explosion, other safety measures, such as an air tight operation of the system; automatic pressure control; and smoke and spark free areas are applied.

### **Applicability**

Vacuum distillation is applicable to sludge containing mercury from the oil and gas production industry, batteries, catalysts, activated carbon filters, thermometers, waste from the dental sector, fluorescent tubes, blasting grit and soil. Different waste streams are separately treated in the vacuum distillation. The capacities of the example installations range from 300 to 600 t/yr of waste containing mercury.

### **Driving force for implementation**

- landfilling is banned for several wastes containing mercury. In comparison with direct landfilling or incineration of the waste containing mercury, the amount of waste is less and contains no mercury and diffusion into the environment is prevented
- the preference order for waste management in accordance with the Waste Framework Directive and the Sixth Environmental Action Programme of the European Union.

### **Example plants**

A thermal soil remediation plant in Sweden, two example plants in the Netherlands for the vacuum distillation treatment. Example plants where pretreatment is applied: one in the Netherlands (shredding of gas discharge lamps) and one in Belgium (end-cut/air-push treatment).

### **Reference literature**

[81, VDI and Dechema, 2002], [150, TWG, 2004], [152, TWG, 2004], [156, VROM, 2004]

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## 4.4. Waste gas treatments

### 4.4.1. Cyclones

#### Description

In all types of cyclones, centrifugal forces are used to separate solid particles or liquid droplets from flue-gases. Cyclone filters are used to remove heavier particulates which 'fall out' as the flue-gases are forced into a rotating motion before they leave the separator again. Two forms exist, e.g. a cyclone or multi-cyclone. The latter separates finer dusts.

#### Achieved environmental benefits

Cyclones are effective for abating particles of sizes  $>10\text{ }\mu\text{m}$ . They are not effective against particle sizes  $<10\text{ }\mu\text{m}$ , which may thus require additional measures, e.g. fabric filters. Some benefits of using a cyclone include:

- efficient over a large concentration range
- collected dust may be re-used in the process.

#### Cross-media effects

Cyclones create a pressure drop in the gas flow requiring a higher energy consumption to overcome this drop and, therefore, lead to higher overall emissions. High wear with abrasive dust.

#### Operational data

Cyclones are relatively reliable. Operational conditions include:

- monitoring of pH, flowrate and the level of scrubber liquors and scrubber pressure drop (pressure drop monitoring with alarm)
- exit concentrations needing to be periodically monitored under different operating conditions.

#### Applicability

This technique may be only used in combination with a bag filter. It is not efficient at separating small particles.

#### Economics

Cyclones are relatively cheap.

#### Example plants

Cyclones are used in hazardous waste fuel preparation, where these are used in the mixing vessel as part of the stabilisation process. They are also used for the treatment of the exhaust gases of Ph-c plants.

#### Reference literature

[55, UK EA, 2001], [122, Eucopro, 2003], [126, Pretz, et al., 2003]

### 4.4.2. Fabric filters

#### Description

The creation of a barrier separates the dust from the flue-gases. Solid particles are trapped by a woven fabric while the gas flow can pass through it. Filter efficiency may be enhanced by pre-coating the filter cloth prior to being brought online.

#### Achieved environmental benefits

- high collection efficiency for both coarse and small particles
- efficient with a large concentration range
- collected dust may be re-used in the process
- high collection efficiency at high temperatures, if special materials, e.g. teflon, are used.

Characteristics	Fabric filter
Input flow range (m <sup>3</sup> /hour)	1000 to 50000
Input concentration (mg/Nm <sup>3</sup> )	100 to 5000
Output concentration (mg/Nm <sup>3</sup> )	<10
Risks	Explosion
Consumption (per tonne waste fuel produced)	
Electricity (kWh)	2.5 to 3.5
Fuel/gas (litre)	-
Reactant (nature and kg)	-
Residues	-
Costs (EUR/t waste fuel produced per year)	
Investment cost	Up to 4
Operation cost	0.15
Maintenance cost	0.1

**Table 4.14: Dust filtration by a fabric filter**  
[122, Eucopro, 2003]

#### Cross-media effects

Cyclones and fabric filters create a pressure drop in the gasflow requiring a higher energy consumption to overcome this drop and therefore this leads to higher overall emissions. A major source of hazardous waste at a number of industries is the dust emanating from air pollution control equipment (e.g. from a baghouse). As with sewerage systems, common dust collectors are utilised in different production areas resulting in a mixing of different types of dust and, thereby, precluding recycling. In some cases, modifications can be made to dust collectors so that each different source of waste goes to a different compartment, thereby, preventing the mixing of different waste types and increasing the recycling potential.

#### Operational data

Insitu cleaning can be achieved by air pulse, counter flow air or mechanical tapping. The reliability highly depends on the filter material. Fabric filters may create a risk of explosion. Fabric filters are equipped with pressure drop monitoring, including alarms and often, with measurement of inlet and exit concentrations. Pressure is often used as an instantaneous surrogate for concentration analysis. From time to time, however, a laboratory control is carried out on the exit concentration in order to quantify the emissions. An opacity meter or particle impingement detector can be used to monitor performance. There need to be a programme in place for the regular cleaning of physical filters.

#### Applicability

Applied for both fugitive emissions and point source emissions to air. Fabric filters are typically used as secondary or tertiary gas cleaning devices in combination with a cyclone or a dry scrubber located upstream. Fabric filters are not generally suitable for use in moisture laden streams or those with acidic, tarry or sticky characteristics. This is due to the adverse effects of fabric 'blinding' and adherence problems.

#### Example plants

Bag filters are used in the preparation of waste fuel. They are also used in the mixing vessel in the stabilisation process in the production of aerosol cans (e.g. for the removal of dust) and for the treatment of the exhaust gases of Ph-c plants.

#### Reference literature

[53, LaGrega, et al., 1994], [55, UK EA, 2001], [122, Eucopro, 2003], [126, Pretz, et al., 2003], [150, TWG, 2004]

### 4.4.3. Biofilters

#### Description

'Biofilter' is the generic term covering all biological oxidation processes taking place in a packed system. This includes conventional trickling filters, bioscrubbers (microbial population supported in scrubber liquor) or biobeds (packed system using soil, peat and bark).

The biofilter consists of an apparatus filled with decomposable material such as compost, bark or a mixture of turf and heather, etc. Micro-organisms (fungi, bacteria, viruses and algae) are resident on the material. The exhaust airflows through the material while the micro-organisms decompose the harmful substances. Water and airflow normally run countercurrently. A biofilter is not a filter in the mechanical sense (i.e. it does not lead to a separation of particles), but it is a reactor where a certain range of harmful substances are metabolised to harmless substances. The desired qualities of a biofilter are outlined in Table 4.15.

Characteristic	Description
Filter media	Biologically active, but reasonably stable
	Organic matter content >60 %
	Porous and friable with 75 – 90 % void volume
	Resistant to water logging and compaction
	Relatively low fines content to reduce gas headloss
	Relatively free of residual odour
	Specifically designed mixtures of materials may be desirable to achieve the above characteristics
Moisture content	50 – 80 % by weight
	Provisions must be made to add water and remove bed drainage
Nutrients	Must be adequate to avoid limitations
	Usually not a problem with aerobic digestion gases because of the high $\text{NH}_3$ content
pH	7 to 8.5
Temperature	Near ambient, 15 – 35 or 40 °C
Gas pretreatment	Humidification could prove to be useful in order to achieve near 100 % inlet gas humidity
	Dust and aerosols may be removed to avoid media plugging, but for most biofilters this is not a problem (unless they have a tissue layer in the bottom)
Gas loading rate	<100 $\text{m}^3/\text{h}\cdot\text{m}^3$ , unless testing supports higher loadings
Gas residence time	30 - 60 seconds, unless testing supports shorter residence time
Media depth	>1m, <2 m
Elimination capacity	Depends on media and compound (typically in the range 10 – 160 $\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ )
Gas distribution	The manifold must be properly designed to present a uniform gas flow to the media

**Table 4.15: Qualities of biofilter media**  
[59, Hogg, et al., 2002]

In contrast to the biofilter, in bioscrubbers the micro-organisms are not fixed in the bioscrubber on organic materials. The biomass swims quasi free in the suspension, which is sprayed on the exhaust gas in a countercurrent flow. The principal difference this brings about is that the absorption of the harmful substances is local and is separated from the metabolism.

In an aerosol can treatment facility, the exhaust air from the different operational parts is led through an air-permeable filter layer by means of ventilators. While the airflows through the filter layer, the degradable contents are decomposed by micro-organisms that populate the filter. In order to ensure that the filter layer remains air-permeable, which is essential for the supply of air oxygen to the micro-organisms, the exhaust air is cleaned beforehand so that solids (dusts) are removed. Simultaneously, cleaning moisturises the exhaust air, which is necessary to prevent drying of the filter layer. The biofilter, thus, represents an aerobic fixed bed reactor for the biochemical decomposition of organic substances. The biofilter, e.g. with an area of 1800  $\text{m}^2$ , can treat an exhaust air stream of approximately 200000  $\text{m}^3/\text{h}$ , which results in a specific filter load area of 111  $\text{m}^3/\text{m}^2/\text{h}$ . Below the biofilter, there are supply areas that are utilised by the different treatment facilities

(provision for treatment and dispatch). This area is designed as a collection tray. Moreover, a stationary foam extinguishing installation is present.

#### Achieved environmental benefits

Reduces odour and VOC emissions from natural compounds and from the synthesis of inorganic compounds (e.g.  $\text{H}_2\text{S}$  and  $\text{NH}_3$ ), aromatic and aliphatic compounds (e.g. acids, alcohols, hydrocarbons). Other compounds that may be degraded are non-chlorinated solvents, mercaptans, amines, amides, aldehydes and ketones. The treatment capacity ranges from 50 - 150  $\text{Nm}^3/\text{h}/\text{m}^2$  depending on the type of pollutant.

Substance (group)	Input concentration ( $\text{mg}/\text{Nm}^3$ )	Output concentration ( $\text{mg}/\text{Nm}^3$ )	Biofilter efficiency (%)
Aldehydes, alkanes			75
Alcohols			90
AOX, aromatic hydrocarbons (benzene)			40
Aromatic hydrocarbons (toluene, xylene)			80
NMVOC			83
PCDD/F			40
Odour			95 – 99
NMVOC (Values in total carbon)	30 – 70	10 – 40	80

**Table 4.16: Biofilter efficiency in MBT waste gas treatment [81, VDI and Dechema, 2002]**

The removal efficiency of a biofilter is determined by the gas residence time in the media bed. Effective residence times typically range from 30 to 60 seconds for most aerobic digestion applications. Studies have reported high removal efficiencies for specific compounds such as  $\text{H}_2\text{S}$  (>99 %), methyl mercaptan, dimethyl disulphide, dimethyl sulphide (>90 %) and various terpenes (>98 %).

Environmental benefits include low energy requirements and the avoidance of potential cross-media transfer of pollutants. Measurements in the practical application of biofilters in physico-chemical treatment plants have shown results of approx. 95 to 98 % degradation for organic solvents, with concentrations in exhaust air to be purified from 400 to 1600  $\text{mg}/\text{Nm}^3$ .

In biological treatment plants, malodorous gases will be fed through a scrubber (e.g. acidic wet scrubber), which reduces the ammonia content to an acceptable level for the biofilter. The biofilter removes odours and any remaining ammonia. The filtering process does not create any compounds that are harmful to the environment and after use, the filter can be treated by composting and additional waste will not be generated. The levels of ammonia and odour after treatment are  $<1 \text{ mg}/\text{m}^3$  and 1000 – 6000  $\text{ouE}/\text{m}^3$  (90 % reduction), respectively.

Table 4.17 and Table 4.18 show the effectiveness of biofilters applied to MBTs.

Parameter	Concentration ( $\mu\text{g}/\text{m}^3$ ) min – max	Effectiveness (%) min – max	Concentration ( $\mu\text{g}/\text{m}^3$ ) min – max	Effectiveness (%) min – max	Concentration ( $\mu\text{g}/\text{m}^3$ ) min – max	Effectiveness (%) min – max
Acetaldehyde	2100 – 2500	78 – 89	46 – 740	89 – 96	4900 – 6100	99
n-Butylacetate	150 – 425	97 – 99	30 – 120	83 – 96	170 – 980	73 – 99
Ethylbenzene	250 – 310	12 – 42	60 – 190	27 – 61	250 – 740	16 – 43
2-Ethyltoluene	180 – 220	33 – 41	25 – 105	14 – 89	80 – 270	25 – 55
3,4-Ethyltoluene	480 – 640	23 – 45	70 – 260	38 – 96	230 – 1000	48 – 77
Limonane	1700 – 4300	29 – 40	810 – 2200	94 – 98	1300 – 3700	30 – 63

Toluene	490 – 550	16 – 39	130 – 280		460 – 1000	7 – 36
m/p-Xylene	850 – 1400	9 – 42	280 – 620	30 – 71	720 – 2000	19 – 45
o-Xylene	260 – 290	23 – 41	60 – 150	7 – 63	160 – 650	20 – 45
Acetone	2450 – 2900	99 – 100	1200 – 2800	99 – 100	4700 – 8200	93 – 97
2-Butanone	960 – 2800	99 – 100	80 – 770	94 – 99	370 – 11000	95 – 100
Ethanol	5200 – 5300	100	88 – 750	94 – 99	14000 – 18000	100
α-Pinene	370 – 700	8 – 44	280 – 790	53 – 83	560 – 930	5 – 39
β-Pinene	330 – 800	12 – 44	120 – 300	53 – 81	230 – 490	38 – 49

**Table 4.17: Concentration ranges for some parameters of the exhaust air from MBTs, showing the retention efficiency of the biofilter for these compounds**  
[132, UBA, 2003], [150, TWG, 2004]

Biological exhaust gas purification processes are able to reduce the exhaust air/exhaust gas contents from municipal waste treatment plants only to a limited extent (typically NMVOC of more than 300 g/t waste). Table 4.18 shows some measurement results from well maintained biofilters with upstream air humidifiers.

Compounds of the exhaust air	Separation efficiency (%)		
	Facility A	Facility B	Facility C
Acetaldehyde	-18 to -99	99	99
n-Butylacetate	83 – 96	73 – 99	97 – 99
Camphor	60 – 88	60 – 90	88 – 91
Dichloromethane	-53 to -80	-300 to -33	43 – 62
Dimethyldisulphide	44 – 78	-55 to -89	10 – 31
2-Hexanone	75 – 80	-	80 – 82
Naphthalene	50 – 75	38 – 93	58 – 82
Phenol	-25 to -79	75 – 88	47 – 94
1,4-Dichlorobenzene	0 – 73	-1900 to -89	-130 to -13
Ethyl benzene	27 – 61	16 – 43	12 – 42
2-Ethyl toluene	14 – 89	25 – 55	33 – 41
3/4-Ethyl toluene	38 – 96	45 – 77	23 – 45
Limonene	94 – 98	30 – 63	29 – 40
Styrene	64 – 89	44 – 66	21 – 50
Toluene	29 – 50	7 – 36	16 – 39
m/p-Xylene	30 – 71	19 – 45	9 – 42
o-Xylene	7 – 63	20 – 45	23 – 41
Acetone	99 – 100	93 – 97	94 – 97
2-Butanone	94 – 99	95 – 100	99 – 100
Ethanol	94 – 99	100	100
Ethylacetate	74 – 93	82	97 – 99
α-Pinene	59 – 83	5 – 39	8 – 44
β-Pinene	53 – 81	38 – 49	12 – 44
Benzene	0 – 17	-	0 – 20
Trichlorethene	-108 to -3	67 – 90	20 – 46
Combinations of air humidifiers and biofilters may provide varying purification power for organic substances of the first and second group			

**Table 4.18: Separation efficiency of organic compounds in the biofilter**  
[132, UBA, 2003]

Table 4.19 gives a summary of current measurement results from the biofilter of an aerosol can treatment facility. Note that other parts of the exhaust air of the treatment process are treated by the in-house high temperature incineration facility.

Component	Average concentration of raw gas	Average concentration of cleaned gas
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Total carbon (FID)	206	49
CHC/CFC	9.69	8.17
Benzene	1.07	0.35
Aromatic compounds	35.4	8.07
Ester, alcohols	80.8	0.57
Results from 2003 and data in mg/m <sup>3</sup>		

**Table 4.19: Raw gas and treated gas by a biofilter in an aerosol can treatment facility [157, UBA, 2004]**

#### Cross-media effects

N<sub>2</sub>O and NO emissions are typically increased. However, it has been demonstrated that the use of an acid scrubber for ammonia (NH<sub>3</sub>) removal prior to biofiltration can reduce potential N<sub>2</sub>O and NO emissions. Methane is neither biodegraded nor produced by the biofilter. Terpenes are produced by the biofilter itself and arise from the degradation of any wooden materials in the biofiltering media. Some references question whether biofilters really decrease VOCs since, they claim, VOCs are actually produced by the biofilter itself.

The degrees of decomposition of the studied biofilters in MBT plants for single compounds are not as high as for several special applications in industry (80 % or >90 %). For non-methane TOC (NMTOC) they achieve on average an efficiency rate of only 40 – 70 %. For methane, the efficiency is close to 0 %. The decomposition efficiency for single compounds in the exhaust gas of MBT plants exhibit good values for NMTOC (e.g. acetone, acetaldehyde, limonene and ethanol), moderate values for BTEX and no reduction for CFCs.

The partly low degradation efficiencies for NH<sub>3</sub> also with a potential inhibition of carbon decomposition, may be improved by the use of acid scrubbers (e.g. sulphuric acid for the absorption of ammonia) instead of neutral scrubbers. The NH<sub>3</sub> emissions will be minimised not only because they are odorous but also because, in the biofilter, close C/N relations of the MBT exhaust air may lead to the formation of NO and N<sub>2</sub>O.

#### Operational data

Biofilters are typically one metre thick of porous material. The material used in the biofilter is usually a mix of green compost typically mounted over a certain structure. These systems are very easy to be built and maintained. High porosity (80 – 90 %), the humidity (60 – 70 %), pH, temperature, and the contact time between the nutrients need to be controlled for good biofilter performance. The humidity in the biofilter can be maintained with a special water system or by humidifying the gas to be purified before it is passed pass through the biofilter.

The NMVOC removal in biofilters strongly depends on the temperature (e.g. weather conditions), which can reduce the efficiency of the biofilter.

In some cases, the materials used for the biofilter media may not be able to fully satisfy the demands for all the essential nutrients of the micro organisms in the biofilter for a longer time. In these cases supplying additional nutrients can significantly increase the efficiency of the biofilter.

The pressure drop is less than 50 mm H<sub>2</sub>O. The surface load per unit area of the biofilters should not exceed approx. 80 Nm<sup>3</sup>/m<sup>2</sup> x h.

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Some issues to consider include:

- incoming air must have a relative humidity of >90 % (this may require the use of a humidifier)
- particulates must be removed
- hot gases may need to be cooled closer to the optimal activity temperature for aerobic micro-organisms, generally 25 to 35 °C and the potential temperature rise across the bed of up to 20 °C needs to be taken into account
- the major operating parameters, such as the off-gas temperature and the back-pressure, need to be checked daily
- the moisture content in the filters needs to be monitored regularly
- a low temperature alarm needs to be fitted to warn of freezing, which can damage the filter and could affect the growth of the microbes
- the packing media must be supported to allow a fast, even airflow without any pressure drop
- the media needs to be removed when it starts to disintegrate, thus affecting the airflow (bark is less resistant than, for example, heather)
- the choice of media and supporting system affects the power requirement for maintaining the airflow, with the power needed to overcome the bed resistance being the largest operational cost
- consideration needs to be given to the effect of a loss of biomass due to the introduction of toxic compounds and a stand-by procedure needs to be developed for such an event.

Even in the case of optimisations (combinations with bio-scrubbers instead of water scrubbers) a low and reliable emission cannot be permanently achieved. For the odorous emissions, a strong reduction can be achieved (with only the filter's innate smell remaining) if an appropriate conditioning of the exhaust air is carried out.

In the case of flue-gas treatment from aerobic digestion of the digestate generated in anaerobic treatments, the concentration of ammonia is rather high (>30 mg/Nm<sup>3</sup>) being in this case necessary to chemically pretreat the flue-gas before it is guided to the biofilter.

#### Applicability

Biofilters are applied for great volumes of exhaust gas streams which carry low organic loads in the particular exhaust gases but which have intensive odours. Concentrations of components to be treated need to be relatively stable for a good performance. Biobeds have been installed on waste treatment sites for the abatement of odorous emissions. Applicable to all types of WWTP.

Biofilters are used for the treatment of exhaust gases in aerosol can treatment facilities, thermal distillative drying of sludge, biological treatment (MBT) plants and Ph-c plants. In Ph-c plants, biofilters are used for the adsorption of the volatile components to compost material and for the biological decomposition of the adsorbed components by micro-organisms in the compost material. If the biofilter is in danger of desiccating, the exhaust air that is to be cleaned has to be moisturised.

Biofilters are suitable only for low polluted exhaust gas streams and are thus only used for the purification of the hall exhaust air streams. Flue-gas cleaning by biofilters or biological cleaning generated in anaerobic digestion plants has been proven to be of value.

#### Economics

Biofiltration and bioscrubbing have lower operating costs than many other air pollution control technologies for treating low concentrations of biodegradable organic pollutants. Bioscrubbers have the higher maintenance cost of the two. Treatment gas flows of more than 1500 Nm<sup>3</sup>/h are considered cost-effective. Investment cost of EUR 550000 for a biofilter applied to treatment of WWTP odours with a flow of 1800 Nm<sup>3</sup>/h.

Characteristics	Value
Input flow range (Nm <sup>3</sup> /h)	<100000
Input VOC concentration (g/Nm <sup>3</sup> )	<1
Efficiency (%)	<90 %



Need for preliminary de-dusting	No
Risks	Destruction of micro-organism
Residues	Yes
Consumption (per tonne waste fuel produced)	
Electricity (kWh)	15
Fuel/gas (kWh)	-
Alternative fuel or biogas	
Reactant (kg)	Barks
Costs	
Investment costs (EUR/t capacity)	10 to 20
Operational costs (EUR/t waste fuel produced)	<1
Maintenance costs (EUR/t waste fuel produced)	<0.25

**Table 4.20: Consumptions and costs of biofilters**  
[122, Eucopro, 2003]

#### Driving force for implementation

Reduction of odour emissions. The German and Austrian Governments have set limit values for MBT facilities for odour emissions with 500 GE/Nm<sup>3</sup> and for VOCs (Austria: 100 g/t treated waste, Germany: 55 g/t treated waste). Furthermore, such systems cannot achieve the TOC emission limit values demanded by some German standards (e.g. less than 55g TOC per tonne of MBT input and a TOC concentration of less than 20 mg/Nm<sup>3</sup>).

#### Example plants

Widely used in the sector. Applied in the treatment of flue-gases from biological treatment plants and from physico-chemical treatment of waste waters and immobilisation. It is also commonly used in other industrial sectors, such as in the chemical, iron and steel, and food industries and in waste water treatment plants. Many examples of the use of biofilters exist in the EU.

#### Reference literature

[52, Ecodeco, 2002], [55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [59, Hogg, et al., 2002], [66, TWG, 2003], [81, VDI and Dechema, 2002], [121, Schmidt and Institute for environmental and waste management, 2002], [122, Eucopro, 2003], [126, Pretz, et al., 2003], [132, UBA, 2003], [135, UBA, 2003], [150, TWG, 2004], [157, UBA, 2004]

### 4.4.4. Scrubbing

#### Description

Absorption techniques are typically called scrubbers. Some techniques include:

- having in place a scrubber system for the major inorganic gaseous releases (e.g. Cl<sub>2</sub>, ClCN, HCl, H<sub>2</sub>S, NH<sub>3</sub>, NO<sub>x</sub>), organic compounds (e.g. VOC) and odour from some unit operations treating certain types of waste (containing these volatile compounds), which have a point discharge for process emissions. In circumstances of highly variable emissions, the installation of a secondary scrubber unit to certain pretreatment systems may be a solution if the discharge is incompatible, or too concentrated for the main scrubbers
- correctly operating and maintaining the abatement equipment, including the handling and disposal of spent scrubber medium.

Water sprays are a commonly used control method for particulate matter emissions. The addition of dust control chemicals such as polymers or acrylics to the water increases the effectiveness of the spraying.

#### Achieved environmental benefits



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Reduces emissions to air of VOC, acids, ammonia, particulates, etc. Increases the efficiency of pollutant adsorption, due to the particle-gas contact (particularly relevant for the removal of acid gases by basic particles injected at the scrubber, if applicable).

#### Cross-media effects

This technique generates liquid effluents and sludge that require further treatment.

Wet scrubbers generate steam plumes. Releases from wet scrubber vents need to be hot enough to avoid visible plume formation in the vicinity of the vent. This is to prevent the condensation or adsorption of environmentally harmful substances by the condensing water vapour. Exhaust gases from a wet scrubber can be heated by the use of waste heat to raise the temperature of the exhaust gases and to prevent immediate condensation on the exit from the vent. This procedure also aids the thermal buoyancy of the plume.

#### Operational data

Usually some level of air monitoring will be carried out, either at the scrubber discharge or at the site boundary. Typically the monitoring of the exit gases from the scrubber systems/filter systems is spasmodic. The assumption is that the abatement systems are fit for this purpose and will reduce the emission to an acceptable background release. Discharge points may be monitored on a quarterly or monthly basis for those acid gases that are expected to be collected.

Water supply and effluent disposal facilities must be available. Monitoring provisions include:

- pH, flowrate and level of scrubber liquors and scrubber pressure drop
- pressure drop monitoring with alarms
- periodically monitoring the exit concentrations under different operating conditions.

There also needs to be a programme in place for the regular changing of absorbent in the absorption units.

#### Applicability

Suitable for high flow, low concentrations (e.g. 1 – 200 mg/Nm<sup>3</sup> VOC), low temperature gas streams and when the pollutant is chemically reactive (or soluble in the case of VOC contaminants).

These techniques are typically applied to point source emissions related to those compounds which result from the collection of gas from a vessel or area and which are passed on either via abatement or direct to a stack or vent. This technique can be used for the treatments of off-gases generated during the loading of storage tanks.

Acid scrubbers are applied to capture the ammonia emissions liberated during the acidic treatment in the re-refining of waste oils. Mineral oil scrubbers are also used to trap VOCs and odours in waste oil treatment facilities.

Hypochlorite or hydrogen peroxide may be used for cyanide scrubbing and odour control. A two-stage system could be utilised, e.g. alkali and oxidiser scrubbers in series. Water supply and effluent disposal facilities need to be available to run these systems. There needs to be a programme for the regular changing of absorbent in the absorption units.

Alkaline potassium permanganate or hypochlorite can be used as oxidisers for the treatment of cyanide compounds.

#### Economics

Table 4.21 below shows a summary of scrubbing costs for emission controls for area sources applied to excavation and removal.

Emission control technique	Material cost (USD/m <sup>2</sup> )	Comments
Water spray	0.001 (varies)	Assuming municipal water cost of 1 USD/1000 litres. Water requires constant re-application. Water

		truck rental: 500 USD/week.
Additives:		Costs vary with chemical use
Surfactant	0.65	
Hygro salt	2.58	
Bitumen/adhesives	0.02	

**Table 4.21: Summary of costs for emission controls for area sources applied to excavation and removal [30, Eklund, et al., 1997]**

#### Example plants

A common use is the treatment of extracted air from the reactor vessel with a scrubber liquor, typically a caustic solution. The process is extensively applied in Ph-c plants (e.g. wet scrubbing). Used as a pretreatment, e.g. before biofilters, for the treatment of the exhaust gases of biological treatment plants.

Pretreatment processes capable of liberating toxic gases tend to have their own scrubbing systems, with the scrubber vent leading into the main site exhaust system, and with the aqueous liquors being treated in the plant.

All of the oxidation systems seen in the UK have their own local scrubber systems, and the residues from both the oxidation and the scrubber solutions are treated in the main plant. Where the plant has a total exhaust system for the site, the exhaust from the oxidation scrubbers typically goes through the main plant exhaust scrubbing system prior to discharge to the air.

Caustic scrubbing is employed to strip hydrogen sulphide in plants treating waste oil.

#### Reference literature

[30, Eklund, et al., 1997], [42, UK, 1995], [55, UK EA, 2001], [56, Babbie Group Ltd, 2002], [86, TWG, 2003], [126, Pretz, et al., 2003], [150, TWG, 2004]

### 4.4.5. Chemical scrubbing

#### Description

Chemical exhaust gas treatment can be one-step or multi-step scrubbing with chemical scrubbers. Up to now, plants of this type have been produced, e.g. as one-step or multi-step carrier material cleaners with controlled pH values in each step or with an addition of oxidants.

#### Achieved environmental benefits

Scrubbers of this type are well suitable for removing single components (e.g. ammonia).

#### Cross-media effects

This scrubber is required for the reduction of N-compounds prior to the subsequent treatment. Multistage exhaust air scrubbers (acid-alkaline), or scrubbing with H<sub>2</sub>O<sub>2</sub>, can only reduce the concentration of certain components (e.g. VOCs) due to the high crude gas concentrations generated especially by recirculating treatments.

#### Applicability

A state-of-the-art technique in biological treatment (MBT) plants is a combination of acid scrubbers and thermal regenerative exhaust gas treatment. The release of the treated exhaust air is carried out via a stack.

#### Driving force for implementation

It is reported that scrubbed gas concentrations required by a German regulation cannot be reached by these systems alone.

#### Example plants

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Currently no information is available on its use as an independent treatment step in biological treatment (MBT) plants. All information in this section corresponds to experiences in other types of plants.

**Reference literature**

[132, UBA, 2003], [150, TWG, 2004]

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## 5. Best available techniques

### Physico-chemical treatments

For the physico-chemical treatment of waste waters, BAT is to:

370. apply the following techniques in physico-chemical reactors (see Section 4.1.2):

- a. clearly defining the objectives and the expected reaction chemistry for each treatment process
- b. assessing each new set of reactions and proposed mixes of wastes and reagents in a laboratory-scale test prior to waste treatment
- c. specifically designing and operating the reactor vessel so that it is fit for its intended purpose
- d. enclosing all treatment/reaction vessels and ensuring that they are vented to the air via an appropriate scrubbing and abatement system
- e. monitoring the reaction to ensure that it is under control and proceeding towards the anticipated result
- f. preventing the mixing of wastes or other streams that contain metals and complexing agents at the same time (see Section 4.1.3).

371. in addition to the generic parameters identified for waste water in BAT number **Error! Reference source not found.**, additional parameters need to be identified for the physico-chemical treatment of waste waters. Some reference is given on this issue in the concluding remark Chapter **Error! Reference source not found.**.

372. apply the following techniques for the neutralisation process (see Section 4.1.3)

- a. ensuring that the customary measurement methods are used
- b. separately storing the neutralised waste water
- c. performing a final inspection of the neutralised waste water after a sufficient storage time has elapsed.

373. apply the following techniques to aid precipitation of the metals in treatment processes (see Section 4.1.4):

- a. adjusting the pH to the point of minimum solubility where the metals will precipitate
- b. avoiding the input of complexing agents, chromates and cyanides
- c. avoiding organic materials that may interfere with precipitation from entering the process
- d. allowing the resulting treated waste to clarify by decantation when possible, and/or by the addition of other dewatering equipment
- e. using sulphidic precipitation if complex agents are present. This technique may increase the sulphide concentration in the treated waste water.

374. apply the following techniques to break-up emulsions (see Section 4.1.5):

- a. testing for the presence of cyanides in the emulsions to be treated. If cyanides are present, the emulsions need a special pretreatment first
- b. setting up simulated laboratory tests.

375. apply the following techniques to oxidation/reduction (see Section 4.1.6):

- a. abating the air emissions generated during the oxidation/reduction
- b. having safety measures and gas detectors in place (e.g. suitable for detecting HCN, H<sub>2</sub>S, NO<sub>x</sub>).

376. apply the following techniques to waste waters containing cyanides (see Section 4.1.7):

- 
- a. destroying the cyanides by oxidation
  - b. adding caustic soda in excess to prevent a decrease in pH
  - c. avoiding the mixing of cyanide wastes with acidic compounds
  - d. monitoring the progress of the reaction using electropotentials.
- 377.apply the following techniques to waste waters containing chromium (VI) compounds (see Section 4.1.8):
- a. avoiding the mixing of Cr(VI) wastes with other wastes
  - b. reducing Cr(VI) to Cr(III)
  - c. precipitating the trivalent metal.
- 378.apply the following techniques to waste waters containing nitrites (see Section 4.1.9):
- a. avoiding mixing nitrite wastes with other wastes
  - b. checking and avoiding nitrous fumes during the oxidation/acidification treatment of nitrites.
- 379.apply the following techniques to waste waters containing ammonia (see Section 4.1.11):
- a. using a dual column air stripping system with an acidic scrubber for waste with ammonia solutions up to 20 w/w-%
  - b. recovering the ammonia in the scrubbers and returning it to the process prior to the settlement stage
  - c. removing the ammonia removed in the gas phase by scrubbing the waste with sulphuric acid to produce ammonium sulphate
  - d. extending any air sampling for ammonia in exhaust stacks or filter press areas to cover the VOCs in filtration and dewatering (see Section 4.1.12).
- 380.link the air space above filtration and dewatering processes to the main abatement system of the plant (see Section 4.1.12)
- 381.add flocculation agents to the sludge and waste water to be treated, to accelerate the sedimentation process and to facilitate the further separation of solids (see Section 4.1.16 for some applicability restrictions identified). To avoid use of flocculation agents, evaporation is better in those cases where it is economically viable (see Section **Error! Reference source not found.**)
- 382.apply rapid cleaning and steam- or high pressure water jet cleaning of the filter apertures of the sieving processes (see Section 4.1.17).
- For the physico-chemical treatment of solid wastes, BAT is to:
- 383.promote the insolubilisation of amphoteric metals, and to reduce the leaching of toxic soluble salts by a suitable combination of water washing, evaporation, recrystallisation and acid extraction (see Section 4.2.1, 4.2.8, 4.2.9) when immobilisation is used to treat solid waste containing hazardous compounds for landfilling
- 384.test the leachability of inorganic compounds, by using the standardised CEN leaching procedures and by applying the appropriate testing level: basic characterisation, compliance testing or on-site verification (see Section 4.2.2)
- 385.restrict the acceptance of wastes to be treated by solidification/immobilisation treatment to those not containing high levels of VOCs, odorous components, solid cyanides, oxidising agents, chelating agents, high TOC wastes and gas cylinders (see Section 4.2.3)
- 386.apply control and enclosure techniques for loading/unloading and enclosed conveyor systems (see Section 4.2.3)
- 387.have an abatement system(s) in place to handle the flow of air, as well as the peak loadings associated with charging and unloading (see Section 4.2.3)
- 388.use at least a solidification, vitrification, melting or fusion process before landfilling solid waste according to techniques in Sections from 4.2.4 to 4.2.7.
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For the physico-chemical treatment of contaminated soil, BAT is to:

389. control the rate of excavation, the amount of contaminated soil area that is exposed, and the duration that soil piles are left uncovered during the excavation and removal of contaminated soil (see Section 4.2.10)

390. use a bench-scale test to determine the suitability of the process to be applied and the best operational conditions for its use (see Section 4.2.11)

391. have collection and control equipment in place such as afterburners, thermal oxidisers, fabric filters, activated carbon, or condensers for the treatment of the gases from thermal treatments (see Section 4.2.11)

report the efficiency achieved during the processes for the different components reduced and also for those that have not been affected by the process (see Section 4.2.3)

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## 6. Emerging techniques

### **Immobilisation of heavy metal chlorides**

A method for the stabilisation of heavy metals wastes generated in the fly ashes vitrification process is based on the batch conversion of heavy metal chlorides with ammonium dihydrogenphosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ). Conversion of heavy metal chlorides into phosphate and its immobilisation in phosphate glass matrix.

### **Ferrous sulphate stabilisation of FGT waste**

#### Description

This stabilization involves a five-step procedure, where the solid material are first mixed with a  $\text{FeSO}_4$  solution and then aerated with atmospheric air at L/S 3 l/kg in order to oxidise Fe(II) to Fe(III) and precipitate iron oxides. This step also includes extraction of soluble salts. The pH of the suspension is then maintained at pH 10 - 11 for about 0.5 to 1 hour to allow dissolved heavy metals to bind to the precipitated iron oxides. The fourth step of the process is dewatering and finally a washing step to exchange remaining water and remove remaining salts. The final stabilised product has a water content of about 50 %.

#### Achieved environmental benefits

The main advantage of this stabilization process is the improved leaching properties of the final product. The leaching characteristics of waste OUT are shown to be very good, and it is expected that low release of heavy metals can be maintained for extended periods of time, as iron oxides are known to endure in geological time frames. The pollution potential of the waste OUT is documented rather detailed and the waste OUT are expected to be less prone to physical disintegration than cement stabilised products because of the fact that most salts are removed. This process stabilises FGT waste and typically have far better leaching properties than cement solidified wastes. This process reduces the amount of waste OUT by about 10 % per dry weight.

#### Cross-media effects

No reutilization strategies have yet been demonstrated, however it has been suggested that the waste OUT can be utilised in road construction after thermal treatment in the combustion chamber of the incinerator. Research activities are currently addressing this issue.

The process produces waste water with high content of salts and relatively low concentrations of metals because Fe(II) is present in the extraction step. The waste water can in most cases be discharged to a marine recipient after a simple treatment or can be deionised by crystallization.

#### Operational data

The process has been demonstrated in pilot scale at a batch plant of about 200 kg dry weight. Parameters like water consumption, mixing of water and materials, Fe(II) oxidation rate, reaction time, pH and pH controlling additive have been optimised. It has been demonstrated that the process is robust with respect to the properties of the waste IN, although some variations in process parameters arise. Typical process data are for one tonne of waste IN: 10 - 50 kg Fe, 20 - 50 minutes aeration, 30 - 60 minutes reaction time,  $\text{H}_2\text{SO}_4$  or  $\text{FeSO}_4$  as pH controlling additive, optimum pH of 10 - 11, and a water consumption of 3 - 4  $\text{m}^3$ . In the current setup, dewatering of the treated material was done with a plate and frame filter press.

#### Applicability

The stabilization unit can be implemented as an integrated part of the incinerator but may also exist as a centralised treatment plant handling residues from several incinerators. The technique has been demonstrated on semidry FGT waste as well as fly ash alone and fly ash combined with sludge from the wet scrubbers (Bamberg product); all with good results.

#### Economics

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Treatment cost is estimated to about EUR 65/tonne with a plant capacity of 20000 tonne/year including investment costs.

#### Driving force for implementation

The main reason for implementing this technology is the very good leaching properties of the waste OUT and the fact that this is expected to last in a long-term perspective.

#### Example plants

The process has only been demonstrated in pilot scale, however it has also been designed in full-scale. No full-scale plants have yet been implemented.

#### Reference literature

[124, Iswa, 2003]

### **Carbon dioxide and phosphate stabilisation of FGT waste**

#### Technical description

Chemical agents used here are CO<sub>2</sub> and/or H<sub>3</sub>PO<sub>4</sub>. This process involves a two-step procedure where the waste IN are first washed at L/S 3 l/kg in order to extract soluble salts. After this the material are dewatered and washed again in a plate and frame filter press at L/S 3 l/kg. The residues are then re-suspended, and CO<sub>2</sub> and/or H<sub>3</sub>PO<sub>4</sub> is added. The stabilization reactions are allowed to occur for 1 - 1.5 hours while pH decreases, and another hour where pH is maintained around pH 7. Finally, the residues are dewatered again and washed at the filter press with another 3 l/kg. The final product has a water content of about 50 %. The use of CO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> as stabilizing agent ensures that heavy metals are bound as carbonates or phosphates.

#### Achieved environmental benefits

It shows very good leaching properties similar to the Ferrox stabilization. Metal carbonates and phosphates are known to generally have low solubilities, and the leaching characteristics of the waste OUT are expected to remain good for extended periods of time. The pollution potential of the waste OUT is documented rather detailed and physical disintegration of the waste OUT in a long-term perspective is expected to be less important than in the case of cement stabilization, because of the fact that most salts are removed. Waste OUTs typically have far better leaching properties than the ones treated with cement. The process reduces the amount of material by about 15 % per dry weight.

#### Cross-media effects

No reutilization strategies have yet been demonstrated. The process produces waste water from first dewatering step. All other process water is recycled in the process. The waste water needs to be treated for dissolved heavy metals in a standard unit, for example using pH adjustment and TMT addition.

#### Operational information

The process has been demonstrated in pilot scale at a batch plant of about 200 kg dry weight. Parameters like water consumption, mixing of water and solid material, CO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> addition, reaction time, pH and pH controlling approach have been optimised. It has been demonstrated that the process is robust with respect to the properties of the waste IN, although some variations in process parameters arise. Depending on waste IN composition, either CO<sub>2</sub> or H<sub>3</sub>PO<sub>4</sub> or both have been used. It has also been demonstrated that flue-gas can be used as CO<sub>2</sub> source.

Typical process data for 1 tonne of waste IN are: 5 - 20 kg of CO<sub>2</sub>, 0 - 40 kg H<sub>3</sub>PO<sub>4</sub> and 3 m<sup>3</sup> H<sub>2</sub>O.

#### Applicability of technique

The stabilization unit can be implemented as an integrated part of the incinerator but may also exist as a centralised treatment plant handling residues from several incinerators. The technique has been demonstrated on semidry FGT waste as well as fly ash alone and fly ash combined with sludge from the wet scrubbers (Bamberg product); all with good results.

#### Economics



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Treatment cost for stabilization is estimated to about EUR 80/tonne with a plant capacity of 20000 tonne/year; including investment costs.

#### Driving force of implementation

The main reason for implementing this technology is the very good leaching properties of the waste OUT and the fact that this is expected to last in a long-term perspective.

#### Examples

The process has only been demonstrated in pilot scale, however it has also been designed in full-scale. No full-scale plants have yet been implemented.

#### References

[124, Iswa, 2003], [152, TWG, 2004]

#### **Treatments of waste contaminated with POPs**

Such type of waste is actually mostly treated by incineration. However other types of technique are emerging as shown in next **Error! Reference source not found..**