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Conference of the Parties to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Dear A Their Disposal Tenth meeting

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Matters related to the implementation of the Convention: scientific and technical matters: technical guidelines

## **Technical guidelines**

Note by the secretariat

Addendum

# Technical guidelines on the environmentally sound co-processing of hazardous wastes in cement kilns

At its tenth meeting, the Conference of the Parties adopted, as amended, the technical guidelines on the environmentally sound management co-processing of hazardous wastes in cement kilns on the basis of the draft contained in document UNEP/CHW.10/6/Add.3, which was prepared by the Government of Chile. The text of the final version of the technical guidelines is set out in the annex to the present document

## **Annex**

Technical guidelines on the environmentally sound co-processing of hazardous wastes in cement kilns

Revised final version (31 October 2011)



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## Glossary

**Aggregates**: Particulate materials used in construction such as sand, gravel, crushed stone and crushed slag.

**Alkali bypass**: A duct located between the feed end of the kiln and the preheater tower. A portion of the kiln exit gas is withdrawn through this and quickly cooled by air or water to avoid excessive alkali, chloride and sulphur build-up on the raw feed. This is also known as kiln exhaust gas bypass.

**Alternative fuels and raw materials (AFR)**: Inputs to clinker production derived from waste streams that contribute energy and/or raw material.

**Alternative fuels**: Wastes with recoverable energy value, used as fuels in a cement kiln, replacing a portion of conventional fossil fuels such as coal. Other terms include: secondary, substitute or wastederived fuels.

**Alternative raw materials**: Waste materials containing useable minerals such as calcium, silica, alumina and iron, which can be used in the kiln to replace raw materials such as clay, shale and limestone. Also known as secondary or substitute raw materials.

**Best available techniques (BAT)**: The most effective methods of reducing emissions and the impact on the environment as a whole.

**Bypass dust**: Dust discarded from the bypass systems of the suspension preheater, precalciner and grate preheater kilns, consisting of fully calcined, kiln feed material.

**Calcination**: Heat-induced removal, or loss of chemically-bound volatiles other than water. In cement manufacture this is the thermal decomposition of calcite (calcium carbonate) and other carbonate minerals that gives a metallic oxide (mainly CaO) plus carbon dioxide.

**Cement kiln dust (CKD)**: The fine-grained, solid, highly alkaline material removed from cement kiln exhaust gas by air pollution control devices. Much of the CKD material is unreacted raw material, including raw mix at various stages of burning and particles of clinker. The term can be used to denote any dust from cement kilns, such as that coming from bypass systems.

**Cement**: Finely ground inorganic material that, when mixed with water, forms a paste that sets and hardens by means of hydration reactions and processes and that, after hardening, retains its strength and stability under water.

**Clinkering**: The thermo-chemical formation of clinker minerals, especially to those reactions occurring above about 1,300° C; also the zone in the kiln where this occurs. Also known as sintering or burning.

**Co-incineration plant**: Under Directive 2000/76/EC of the European Parliament and of the Council, any stationary or mobile plant whose main purpose is the generation of energy or the production of material products and which uses wastes as a regular or additional fuel; or in which waste is thermally treated for the purpose of disposal. If co-incineration takes place in such a way that the main purpose of the plant is not the generation of energy or production of material products but rather the thermal treatment of waste, the plant shall be regarded as an incineration plant.

**Co-processing**: The use of suitable waste materials in manufacturing processes for the purpose of energy and/or resource recovery and resultant reduction in the use of conventional fuels and/or raw materials through substitution.

**Destruction and removal efficiency (DRE)**: Efficiency in destruction and removal of a given organic compound. Mathematically, DRE is calculated as follows:

$$DRE = [(W_{in} - W_{out stack})/W_{in}] \times 100$$

where  $W_{\rm in}$  is the mass feed rate of one principal organic hazardous constituent (POHC) in the waste stream fed to the kiln, and  $W_{\rm out\, stack}$  is the mass emission rate of the same POHC in the exhaust emissions prior to release to the atmosphere.

**Destruction efficiency (DE)**: A measure of the percentage of a given organic compound that is destroyed by the combustion process. Mathematically, DE is calculated as follows:

DE = 
$$[(W_{in} - W_{out combustion chamber})/W_{in}] \times 100$$

where  $W_{\rm in}$  is the mass feed rate of one principal organic hazardous constituent (POHC) in the waste stream fed to the kiln, and  $W_{\rm out\ combustion\ chamber}$  is the mass emission rate of the same POHC leaving the kiln (upstream of all air pollution control equipment). The DE represents the fraction of the organics

entering a kiln, which is actually destroyed; the DRE represents the fraction of the organics entering a kiln and emitted from the stack to the atmosphere.

**Dry process**: Process technology for cement production. In the dry process, the raw materials enter the cement kiln in a dry condition after being ground to a fine powder called the raw meal. The dry process consumes less energy than the wet process, where water is added to the raw materials during grinding to form slurry.

**Emissions testing**: Manual collection of stack gas samples, followed by chemical analysis to determine pollutant concentrations.

**Heating** (calorific) value: The heat per unit mass produced by complete combustion of a given substance. Calorific values are used to express the energy values of fuels, usually expressed in megajoules per kilogram (MJ/kg).

**Higher heating (calorific) value (HHV)**: Maximum amount of energy that can be obtained from the combustion of a fuel, including the energy released when the steam produced during combustion is condensed. Also called the gross heat value.

**Kiln line**: The part of the cement plant that manufactures clinker; comprises the kiln itself, any preheaters and precalciners and the clinker cooler apparatus.

**Kiln**: The heating apparatus in a cement plant for manufacturing clinker. Unless otherwise specified, it may be assumed to refer to a rotary kiln.

**Lower heating (calorific) value (LHV)**: The higher heating value less the latent heat of vaporization of the water vapour formed by the combustion of the hydrogen in the fuel. Also called the net heat value.

**Precalciner**: A kiln line apparatus, usually combined with a preheater, in which partial to almost complete calcination of carbonate minerals is achieved ahead of the kiln itself, and which makes use of a separate heat source. A precalciner reduces fuel consumption in the kiln, and allows the kiln to be shorter, as it no longer has to perform the full calcination function.

**Preheater**: An apparatus for heating the raw mix before it reaches the dry kiln itself. In modern dry kilns, the preheater is commonly combined with a precalciner. Preheaters use hot exit gases from the kiln as their heat source.

**Pre-processing**: Alternative fuels and/or raw materials not having uniform characteristics must be prepared from different waste streams before being used as such in a cement plant. The preparation process, or pre-processing, is needed to produce a waste stream that complies with the technical and administrative specifications of cement production and to guarantee that environmental standards are met

**Pyroprocess system**: Includes the kiln, cooler, and fuels combustion equipment.

**Raw mix/meal/feed**: The crushed, ground, proportioned, and thoroughly mixed raw material-feed to the kiln line.

**Recovery**: Any operation where waste is serving a useful purpose by replacing other materials that would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy.

**Rotary kiln**: A kiln consisting of a gently inclined, rotating steel tube lined with refractory brick. The kiln is fed with raw materials at its upper end and heated by flame from, mainly, the lower end, which is also the exit end for the product (clinker).

**Trial burn**: Emissions testing performed for demonstrating compliance with the destruction and removal efficiency (DRE) and destruction efficiency (DE) performance standards and regulatory emission limits; is used as the basis for establishing allowable operating limits.

**Vertical shaft kiln (VSK)**: A vertical, cylindrical or chimney-type kiln, heated from the bottom, fed either with a batch or continuous charge consisting of a specific mix of fuel and raw materials. Based on a black-meal process, which prevents the use of alternative fuels, it is generally considered obsolete for cement manufacture.

## Abbreviations and acronyms

ACGIH American Conference of Governmental Industrial Hygienists (http://www.acgih.org)

ASTM American Society for Testing and Materials (http://www.astm.org/)

BAT Best Available Technique

BAT-AEL BAT Associated Emission Level
BEP Best Environmental Practice

BREF Reference Document on Best Available Techniques (as published by EIPPCB,

http://eippcb.jrc.es/)

CCME Canadian Council of Ministers of the Environment (http://www.ccme.ca/)

CEM Continuous Emission Monitoring Systems

CEN European Committee for Standardization (http://www.cen.eu/)

CKD Cement Kiln Dust

CLM BREF Reference Document on Best Available Techniques for the Cement, Lime and

Magnesium Oxide Manufacturing (as published by EIPPCB, http://eippcb.jrc.es/)

DE Destruction Efficiency

DRE Destruction and Removal Efficiency

EA Environment Agency of England and Wales (http://www.environment-

agency.gov.uk/)

EIPPCB European Integrated Pollution Prevention Control Bureau (http://eippcb.jrc.es/)

EPA United States Environmental Protection Agency (http://www.epa.gov/)

ESM Environmentally Sound Management

GTZ Deutsche Gesellschaft für Technische Zusammenarbeit GmbH, renamed Deutsche

Gesellschaft für Internationale Zusammenarbeit GmbH (http://www.giz.de/)

ICP Inductively coupled plasma

IOELV Indicative Occupational Exposure Limit Value

IPPC Integrated pollution prevention and control

I-TEQ International Toxic Equivalent
MSDS Material Safety Data Sheets

NIOSH National Institute for Occupational Health and Safety of the United States

(http://www.cdc.gov/niosh/)

OECD Organisation for Economic Co-operation and Development (http://www.oecd.org/)

OSHA Occupational Safety and Health Administration of the United States

(http://www.osha.gov/)

PAH Polycyclic Aromatic Hydrocarbon

PCB Polychlorinated Biphenyl

PCDD Polychlorinated Dibenzo-p-Dioxin
PCDF Polychlorinated Dibenzo-Furan

PEL Permissible exposure limit
PIC Product of incomplete combustion

POHC Principal organic hazardous constituent

POP Persistent organic pollutant
PPE Personal protective equipment

QA Quality assurance

QC Quality control

SBC Secretariat of the Basel Convention (http://www.basel.int/)

TEQ Toxic equivalent
THC Total hydrocarbon
TLV Threshold limit value
TOC Total organic compounds

UNEP United Nations Environment Programme (http://www.unep.org/)

VOC Volatile organic compound

WAP Waste analysis plan

WBCSD World Business Council for Sustainable Development (http://www.wbcsd.org/)

XRF X-Ray fluorescence

## I. Introduction

## A. Scope

- 1. Current technical guidelines for environmentally sound co-processing of hazardous waste as alternative fuels and raw materials for use in cement kilns conform to decisions VIII/17, IX/17 and X/8 of the Conference of the Parties to the Basel Convention on the Control of Transboundary Movement of Hazardous Wastes and Their Disposal and decision OEWG-VII/9 of the Open-ended Working Group of the Basel Convention.
- 2. Co-processing of wastes in properly controlled cement kilns provides energy and materials recovery while cement is being produced, offering an environmentally sound recovery option for many waste materials. As countries strive for greater self-sufficiency in hazardous waste management, particularly in developing countries that may have little or no waste management infrastructure, properly controlled co-processing can provide a practical, cost-effective and environmentally preferred option to landfill and incineration. In general, co-processing of waste in resource-intensive processes can be an important element in a more sustainable system of managing raw materials and energy.
- 3. Co-processing is the use of alternative fuel and/or raw materials for the purpose of energy and/or resource recovery. This differs from co-incineration, the production of materials while using wastes as fuel or the plant in which waste is thermally treated for the purpose of disposal.
- 4. While these technical guidelines refer to hazardous waste as defined by the Basel Convention, because the selection of wastes suitable for co-processing in cement kilns is influenced by many factors other than hazardous characteristics exhibited by the waste itself, some guidance may also apply to non hazardous waste. The guidelines do not cover the use of waste as a substitute for clinker in cement production.

## B. Overview of cement manufacturing

- 5. Cement is a non-metallic, inorganic fine powder, which sets and hardens when mixed with water; it is the key constituent of concrete. Cement production involves the heating, calcining and sintering (also known as 'burning' or 'clinkering') of an accurate mix of calcareous and argillaceous materials. This produces cement clinker, which is then cooled and ground with additives such as gypsum (a setting retardant) to make cement.
- 6. Clinker typically has a composition of about 67% CaO, 22% SiO2, 5% Al2O3, 3% Fe2O3 and 3% of other components (Taylor, 1997). Naturally occurring calcareous deposits, such as limestone, marl or chalk, consisting essentially of calcium carbonate (CaCO3), are required to yield calcium oxide (CaO). Clay or shale typically provides the remaining components. The raw materials used in the cement production process naturally contain metals and halogens, in amounts that depend on the geological formations from which the raw materials are mined; some materials may also contain organic carbon such as kerogens. Likewise, coal can contain significant quantities of sulphur, trace metals and halogens, their concentrations being dependent on the area in which the coal was mined. Average values and range of trace element concentrations in primary fuels and conventional raw materials can be found in Mantus (1992), Achternbosch et al. (2003) and WBCSD (2005).
- 7. With the exception of vertical shaft kilns (VSK) still used in certain geographical areas (mainly China and India) (CPCB, 2007; Höhne and Ellermann, 2008), cement clinker is predominantly burnt in rotary kilns, where heating of the raw meal can take place in one of four different types of arrangements: 'dry', 'semi-dry', 'semi-wet', or 'wet' processes. In Europe and the United States, about 90 per cent and 80 per cent, respectively, of cement production is from dry process kilns (EIPPCB, 2010; United States EPA, 2007). The wet process, on the other hand, remains dominant in the former Soviet Union and Australia and New Zealand and is still significant in Canada, India, Latin America and Africa (Watson et al., 2005).
- 8. Cement manufacture is resource intensive typically 1.5–1.7 tonnes of raw material is quarried per tonne of clinker produced (Szabó et al, 2003). In addition, manufacturing requires substantial energy with temperatures of over 2,000° C required in the cement kilns. Each ton of cement produced typically requires 60–130 kilograms of fuel oil, or its equivalent, and about 105 KWh of electricity (Loréa, 2007). On average, energy costs of fuel and electricity represent 40 per cent of cement manufacturing costs (EIPPCB, 2010).
- 9. Further detailed information about the cement manufacturing process may be found, among others, in United States EPA (1993), CEMBUREAU (1999a), (van Oss, 2005) and EIPPCB (2010).

- 10. In 2008, global cement production was estimated at 2.9 billion tonnes, with China responsible for about half of the world's production (Da Hai et al., 2010; United States Geological Survey, 2009). Estimates put world cement consumption reaching 3.4 billion tonnes by 2020, with the corresponding increases in energy, raw materials needs and pollutant mass emissions (Degré, 2009).
- 11. Clinker burning is the most important phase of the production process in terms of the environmental impact associated with cement manufacture. Depending on the specific production processes, cement plants cause emissions to air and waste emissions to land. This includes cement kiln dust (CKD), where recycling back into the production process may be restricted. Emissions to water may also occur in atypical cases. Noise and odours can also have an effect.
- 12. The key pollutants released to air are particulates, nitrogen oxides (NOX) and sulphur dioxide (SO2) (EIPPCB, 2010). Other emissions include: carbon oxides (CO, CO2), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCCDs/PCDFs), volatile organic compounds (VOC), metals and their compounds, hydrogen chloride (HCl) and hydrogen fluoride (HF). The type and quantity of air emissions depend on varying parameters, for example, the raw materials and fuels used and the type of process.
- 13. Cement manufacturing is also associated with impacts of resource extraction (fossil fuel, limestone and other minerals) upon environmental quality, biodiversity, landscape aesthetics and the depletion of non-renewable or slowly renewable resources, such as fossil fuels or groundwater (Battelle, 2002).

## C. Co-processing of hazardous waste in cement kilns

- 14. Co-processing in resource-intensive industries involves the use of waste in manufacturing processes for the purpose of energy and resource recovery, reducing the use of conventional fuels and raw materials through substitution. In particular, the co-processing of hazardous waste in cement kilns allows the recovery of the energy and mineral value from waste while cement is being produced.
- 15. Co-processing is a sustainable development concept based on the principles of industrial ecology focusing on the potential role of industry in reducing environmental burdens throughout the product life cycle (Mutz et al., 2007; Karstensen, 2009a). One of the most important goals of industrial ecology is to make one industry's waste another's raw material (OECD, 2000). Within the cement industry the use of wastes as fuel and raw materials is a positive, forward-thinking example.
- 16. Co-processing wastes serve a useful purpose in replacing materials that would have otherwise been used in cement manufacturing, thereby conserving natural resources. Under the Basel Convention this constitutes an operation "which may lead to resource recovery1, recycling, reclamation, direct reuse or alternative uses" under categories R1 ("use as a fuel or other means to generate energy") and/or R5 ("recycling/reclamation of other inorganic materials") of part B of Annex IV to the Convention.
- 17. The Basel Convention places obligations on countries that are parties to ensure the environmentally sound management (ESM) of hazardous and other wastes. In this regard, the guiding principle for securing a more sustainable waste management system is the waste hierarchy of management practices, including giving due consideration to the protection of the environment and human health. This places waste prevention or avoidance in a preeminent position. Where waste avoidance is not possible, reuse, recycling and recovery of waste are preferable alternatives to non-recovery operations. As an example, co-processing in cement kilns provides an environmentally sound resource recovery option preferable to landfilling and incineration.
- 18. Fossil fuels and raw materials have been successfully substituted by various types of wastes in cement kilns in Australia, Canada, Europe, Japan and the United States of America since the beginning of the 1970s (GTZ/Holcim, 2006). The experiences of various jurisdictions with the use of hazardous and non-hazardous wastes as fuels and/or raw materials in cement kilns is reviewed by CCME (1996), EA (1999a), Twigger et al. (2001) and Karstensen (2007a), among others.
- 19. Although the practice varies among individual plants, cement manufacture can consume significant quantities of wastes as fuel and non-fuel raw materials. This consumption reflects the process characteristics in clinker kilns, which ensure the complete breakdown of the raw materials into their component oxides and the recombination of the oxides into the clinker minerals. The essential

<sup>1</sup> In accordance with the European Court of Justice's judgement of 13 February 2003 delivered in case C-458/00.

process characteristics for the use of hazardous and other wastes, fed to the kiln via appropriate feed points, can be summarized as follows (EIPPCB, 2010):

- (a) Maximum temperatures of approximately 2,000° C (main firing system, flame temperature) in rotary kilns;
  - (b) Gas retention times of about 8 seconds at temperatures above 1,200° C in rotary kilns;
  - (c) Material temperatures of about 1,450° C in the sintering zone of rotary kilns;
  - (d) Oxidising gas atmosphere in rotary kilns;
- (e) Gas retention time in the secondary firing system of more than 2 seconds at temperatures above  $850^{\circ}$  C; in the precalciner, the retention times are correspondingly longer and temperatures are higher
  - (f) Solids temperatures of 850° C in the secondary firing system and/or the calciner;
- (g) Uniform burnout conditions for load fluctuations due to the high temperatures at sufficiently long retention times;
- (h) Destruction of organic pollutants because of high temperatures at sufficiently long retention times;
  - (i) Sorption of gaseous components such as HF, HCl, and SO<sub>2</sub> on alkaline reactants;
  - (j) High retention capacity for particle-bound heavy metals;
- (k) Short retention times of exhaust gases in the temperature range known to lead to formation of PCDDs/PCDFs;
- (l) Simultaneous material recycling and energy recovery through the complete use of fuel ashes as clinker components;
- (m) Product-specific wastes are not generated due to a complete material use into the clinker matrix (although some cement plants dispose of CKD or bypass dust);
- (n) Chemical-mineralogical incorporation of non-volatile heavy metals into the clinker matrix.
- 20. The numerous potential benefits possible through the use of hazardous and other wastes in cement manufacturing processes by the recovery of their material and energy content include: the recovery of the energy content of waste, conservation of non-renewable fossil fuels and natural resources, reduction of CO2 emissions, reduction in production costs, and use of an existing technology to treat hazardous wastes (see, for example, Mantus, 1992; Battelle, 2002; WBCSD, 2005; Karstensen, 2007b).
- 21. The most direct benefit is the embodied energy in alternative fuels that is harnessed by cement plants as this replaces demand for fossil fuels (Murray and Price, 2008). Fossil fuel dependency is reduced and savings are made through resource conservation. The amount of fossil fuel demand that is displaced depends, among other factors, on the calorific value and water content of the alternative fuel.
- 22. In addition, the fuel substitutes may have lower carbon contents (on a mass basis) than fossil fuels, and alternative raw materials that do not require significantly more heat (and fuel) to process, may contribute part of the CaO needed to make clinker from a source other than CaCO3 (Van Oss, 2005). Therefore, another direct benefit of waste co-processing in cement manufacturing is a potential reduction in CO2 emissions. Integrating cement kiln co-processing within an overall waste management strategy may offer a potential to reduce net global CO2 emissions relative to a scenario where waste is combusted in an incinerator without energy recovery (EA, 1999b; CEMBUREAU, 2009).
- 23. The use of alternative materials to replace traditional raw materials reduces the exploitation of natural resources and the environmental footprint of such activities (WBCSD, 2005; CEMBUREAU, 2009).
- 24. Cost savings that are derived from the use of pre-existing kiln infrastructure to co-process waste that cannot be minimized or otherwise recycled avoid the need to invest in purpose-built incinerators or landfill facilities (GTZ/Holcim, 2006; Murray and Price, 2008). Unlike dedicated waste incinerators, ash residues from hazardous waste materials co-processed in cement kilns are incorporated into the clinker so there are no end products that require further management.

- 25. It is of utmost importance that co-processing of hazardous waste in cement kilns is performed only according to best available techniques (BAT)2 while meeting requirements set out for input, process and emission controls. In this context, the prevention or minimization of the formation and subsequent release of unintentional persistent organic pollutants (POPs) is the subject of Article 5 of the Stockholm Convention on Persistent Organic Pollutants. Guidance on BAT and provisional guidance on best environmental practices (BEP) have been published by the Convention Secretariat and adopted by the Conference of the Parties to the Convention in its decision SC-3/5. Other sources of particular relevance are the European Commission's BAT reference documents (BREFs) which have been issued for cement, lime and magnesium oxide manufacturing (EIPPCB, 2010), waste treatment industries (EIPPCB, 2006), and on the general principles of monitoring (EIPPCB, 2003).
- 26. BREFs present the results of an exchange of information coordinated by the European Commission and carried out under Directive 2008/1/EC (Integrated Pollution Prevention and Control Directive), between European Union member States, industries concerned and non-governmental environmental organizations. These provide guidance to European Union Member States on BAT and associated emission levels, in addition to providing other useful sector-specific information.
- 27. An appropriate national legal and regulatory framework within which hazardous waste management activities can be planned and safely carried out should ensure that the waste is properly handled through all operations, from the point of generation until its disposal. Parties to the Basel and Stockholm conventions should also examine national controls, standards and procedures to ensure that they are in agreement with the conventions and with their obligations under them, including those that pertain to ESM of hazardous wastes.
- 28. Co-processing of hazardous waste should be performed only in cement kilns that fully meet permit requirements and follow applicable local regulations. For example, for facilities co-processing hazardous and other wastes located in the European Union, the requirements of Directive 2000/76/EC (Waste Incineration Directive; to be replaced in January 2014 by Directive 2010/75/EU on industrial emissions) and the Directive 2008/98/EC (Waste Framework Directive) apply.

# II. Relevant provisions of the Basel Convention and International Linkages

## A. General provisions of the Basel Convention

- 29. The Basel Convention, which entered into force on 5 May 1992, stipulates that any transboundary export, import or transit is permitted only when both the movement and the disposal of the hazardous wastes are environmentally sound.
- 30. Paragraph 1 of Article 2 ("Definitions") of the Basel Convention defines wastes as "substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law". Paragraph 4 of Article 2 defines disposal as "any operation specified in Annex IV" to the Convention. Paragraph 8 defines the environmentally sound management of hazardous wastes or other wastes as "taking all practicable steps to ensure that hazardous wastes or other wastes are managed in a manner which will protect human health and the environment against the adverse effects which may result from such wastes".
- 31. Paragraph 1 of Article 4 ("General obligations") establishes the procedure by which parties exercising their right to prohibit the import of hazardous wastes or other wastes for disposal shall inform the other parties of their decision. Paragraph 1 (a) states: "Parties exercising their right to prohibit the import of hazardous or other wastes for disposal shall inform the other Parties of their decision pursuant to Article 13". Paragraph 1 (b) states: "Parties shall prohibit or shall not permit the export of hazardous or other wastes to the Parties which have prohibited the import of such waste when notified pursuant to subparagraph (a)."
- 32. Paragraphs 2 (a)–(d) of Article 4 set out key provisions of the Convention pertaining to ESM, waste minimization and disposal practices that mitigate adverse effects on human health and the environment:

VSKs should not be considered as an option for BAT (UNEP, 2007). Many VSKs plants have virtually no environmental controls in place, and the nature of the technology precludes effective use of modern dust (and other emission) controls (Karstensen, 2006a).

"Each Party shall take appropriate measures to:

- (a) Ensure that the generation of hazardous wastes and other wastes within it is reduced to a minimum, taking into account social, technological and economic aspects;
- (b) Ensure the availability of adequate disposal facilities, for the environmentally sound management of hazardous wastes and other wastes, that shall be located, to the extent possible, within it, whatever the place of their disposal;
- (c) Ensure that persons involved in the management of hazardous wastes or other wastes within it take such steps as are necessary to prevent pollution due to hazardous wastes and other wastes arising from such management and, if such pollution occurs, to minimize the consequences thereof for human health and the environment;
- (d) Ensure that the transboundary movement of hazardous wastes and other wastes is reduced to the minimum consistent with the environmentally sound and efficient management of such wastes, and is conducted in a manner which will protect human health and the environment against the adverse effects which may result from such movement."

#### B. General considerations on environmentally sound management

33. ESM is a broad policy concept without a clear universal definition at the current time. However, provisions pertaining to ESM as it applies to hazardous wastes within the Basel and Stockholm conventions, and also the Organisation for Economic Co-operation and Development (OECD) core performance elements (discussed in the next three subsections), provide international direction that is also supportive of ESM efforts under way in various countries and among industrial sectors.

#### 1. Basel Convention

- 34. In paragraph 8 of its Article 2, the Basel Convention defines ESM of hazardous wastes or other wastes as "taking all practicable steps to ensure that hazardous wastes or other wastes are managed in a manner which will protect human health and the environment against adverse effects which may result from such wastes".
- 35. In paragraph 2 (b) of Article 4, the Convention requires each party to take the appropriate measures to "ensure the availability of adequate disposal facilities for the environmentally sound management of hazardous or other wastes, that shall be located, to the extent possible, within it, whatever the place of their disposal", while in paragraph 2 (c) it requires each party to, "ensure that persons involved in the management of hazardous wastes or other wastes within it take such steps as are necessary to prevent pollution due to hazardous wastes and other wastes arising from such management and, if such pollution occurs, to minimize the consequences thereof for human health and the environment".
- 36. In paragraph 8 of Article 4, the Convention requires that "hazardous wastes or other wastes, to be exported, are managed in an environmentally sound manner in the State of import or elsewhere. Technical guidelines for the environmentally sound management of wastes subject to this Convention shall be decided by the Parties at their first meeting". The present guidelines are intended to give a more precise definition of ESM in the context of co-processing hazardous wastes in cement kilns, including appropriate treatment and disposal methods for these waste streams.
- 37. Several key principles were articulated in the 1994 framework document on the preparation of technical guidelines for the environmentally sound management of wastes subject to the Basel Convention. It recommends a number of legal, institutional and technical conditions (ESM criteria) such as:
- (a) A regulatory and enforcement infrastructure to ensure compliance with applicable regulations;
- (b) Sites or facilities are authorized and are of an adequate standard of technology and pollution control to deal with hazardous wastes in the way proposed, in particular taking into account the level of technology and pollution control in the exporting country;
- (c) Operators of sites or facilities at which hazardous wastes are managed are required, as appropriate, to monitor the effects of those activities;
- (d) Appropriate action is taken in cases where monitoring gives indications that the management of hazardous wastes has resulted in unacceptable releases;
- (e) People involved in the management of hazardous wastes are capable and adequately trained in their capacity.

- 38. The 1999 Basel Declaration on Environmentally Sound Management, adopted by the Conference of the Parties to the Basel Convention at its fifth meeting, calls upon the parties to enhance and strengthen their efforts and cooperation to achieve ESM through prevention, minimization, recycling, recovery and disposal of hazardous and other wastes subject to the Convention, taking into account social, technological and economic concerns; and through further reduction of transboundary movements of hazardous and other wastes subject to the Convention.
- 39. The Basel Declaration lists a number of activities that should be carried out in this context, including:
  - (a) Identification and quantification of the types of waste being produced nationally;
- (b) Best practice approach to avoid or minimize the generation of hazardous wastes and reduce their toxicity, such as the use of cleaner production methods or approaches;
- (c) Provision of sites or facilities authorized as environmentally sound to manage wastes and, in particular, hazardous wastes.

#### 2. Stockholm Convention

40. Although the term "environmentally sound management" is not defined in the Stockholm Convention, environmentally sound methods for disposal of wastes consisting of, containing or contaminated with POPs are to be determined by the Conference of Parties in cooperation with the appropriate bodies of the Basel Convention.

#### 3. Organisation for Economic Co-operation and Development

- 41. OECD has adopted a recommendation on ESM of wastes that covers such items as the core performance elements of ESM guidelines applying to waste recovery facilities, including elements of performance that precede collection, transport, treatment and storage; and elements subsequent to storage, transport, treatment and disposal of pertinent residues. The core performance elements state that the facility should have the following:
  - (a) An applicable environmental management system (EMS) in place;
- (b) Sufficient measures in place to safeguard occupational and environmental health and safety;
  - (c) An adequate monitoring, recording and reporting programme;
  - (d) An appropriate and adequate training programme for its personnel;
  - (e) An adequate emergency plan;
  - (f) An adequate plan for closure and after-care.

## III. General guidance on environmentally sound co-processing in cement kilns

#### A. Principles of co-processing in cement manufacturing

- 42. Hazardous and non hazardous waste co-processing in cement manufacturing, when carried out in a safe and environmentally sound manner, is recognized as having far-reaching environmental benefits (CEMBUREAU, 1999b; 2009). To avoid situations in which poor planning may result in increased polluting emissions or the failure to accord priority to a more environmentally preferable waste management practice, a set of general principles were developed by Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH and Holcim Group Support Ltd. (GTZ/Holcim, 2006). These principles (Table 1) provide a comprehensive, concise summary of the key considerations for co-processing project planners and stakeholders.
- 43. The World Business Council for Sustainable Development (WBCSD, 2005) has also outlined similar principles. Karstensen (2008a, 2009a) laid out general requirements specific to cement kilns co-processing hazardous wastes on a routine basis, adopted by the Department of Environmental Affairs and Tourism of the Government of South Africa (2009) in the framework for the implementation of co-processing in cement production (table 2).

Table 1
General principles for co-processing of hazardous and other wastes in cement kilns

Principle	Description
The waste management hierarchy should be respected	<ul> <li>Waste should be co-processed in cement kilns where more ecologically and economically robust methods of recovery are not available</li> <li>Co-processing should be considered an integrated part of waste management</li> <li>Co-processing should be in line with the Basel and Stockholm Conventions and other relevant international environmental agreements</li> </ul>
Additional emissions and negative impacts on human health must be avoided	<ul> <li>Negative effects of pollution on the environment and human health must be prevented or kept at a minimum</li> <li>Air emissions from cement kilns co-processing waste cannot be statistically higher than those not involved in co-processing waste</li> </ul>
The quality of the cement must remain unchanged	<ul> <li>The product (clinker, cement, concrete) must not be used as a sink for heavy metals</li> <li>The product must not have any negative impacts on the environment (for example, as determined by leaching tests)</li> <li>The quality of the product must allow for end-of-life recovery</li> </ul>
Companies that coprocess must be qualified	<ul> <li>Assure compliance with all laws and regulations</li> <li>Have good environmental and safety compliance records</li> <li>Have personnel, processes, and systems in place committed to protecting the environment, health, and safety</li> <li>Be capable of controlling inputs to the production process</li> <li>Maintain good relations with public and other parties involved in local, national and international waste management schemes</li> </ul>
Implementation of co-processing must consider national circumstances	<ul> <li>Country-specific requirements and needs must be reflected in regulations and procedures</li> <li>Implementation must allow for the build-up of the required capacity and the set-up of institutional arrangements</li> <li>Introduction of co-processing must be in line with other change processes in the waste management structure of a country</li> </ul>

Source: GTZ/Holcim (2006)

Table 2

#### General requirements for co-processing of hazardous and other wastes in cement kilns

- (1) An approved environmental impact assessment and all required national/local licenses, permits, authorisations and permissions
- (2) Compliance with all relevant national and local regulations
- (3) Suitable location, technical infrastructure, storage and processing equipment
- (4) Reliable and adequate power and water supply
- (5) Application of BAT for air emissions pollution prevention and control, along with continuous emission monitoring to ensure compliance with regulation and permits (verified through regular baseline monitoring)
- (6) Exit gas conditioning/cooling and low temperatures (< 200°C) in the air pollution control device to prevent dioxin formation
- (7) Clear management and organisational structure with unambiguous responsibilities, reporting lines and feedback mechanism
- (8) An error reporting system (incident preventive and corrective action) for employees
- (9) Qualified and skilled employees to manage wastes and health, safety and environmental issues
- (10) Adequate emergency and safety equipment and procedures, and regular training
- (11) Authorised and licensed collection, transport and handling of hazardous wastes
- (12) Safe and sound receiving, storage and feeding of hazardous wastes
- (13) Adequate laboratory facilities and equipment for hazardous waste acceptance and feeding control
- (14) Adequate record keeping of wastes and emissions

- (15) Adequate product quality control routines
- (16) Implementation of an environmental management system (EMS) including a continuous improvement programme
- (17) Independent audits (government sanctioned or otherwise), emission monitoring and reporting
- (18) Stakeholder dialogues with local community and authorities, and mechanisms for responding to comments and complaints
- (19) Open disclosure of performance and compliance verification reports on a regular basis

Source: Adapted from South African Government Department of Environmental Affairs and Tourism (2009) and Karstensen (2009a)

## B. Considerations when selecting wastes for co-processing

- 44. The strict quality controls for cement products and the nature of the manufacturing process mean that only carefully selected hazardous and non-hazardous waste is suitable for use in coprocessing (WBCSD, 2005). In the BREF issued for this sector by the European Commission, the best available technique is to carry out a careful selection and control of all substances entering the kiln to avoid and/or reduce emissions (EIPPCB, 2010).
- 45. When deciding on the suitability of a hazardous waste for co-processing the chemical composition of the cement and the risk of damage to the environment or public health and safety must be taken into account. It is recommended that a life-cycle approach of the complete recovery chain of hazardous wastes be used to assess the available recovery operations.
- 46. As a basic rule, the use of hazardous waste in cement manufacturing should add value to the process, for example the heating value and the material value of the mineral composition, while meeting applicable regulations and permit requirements. Although wastes with a high metal content will generally not be suitable for co-processing, because the operating characteristics of cement plants are variable the precise composition of acceptable wastes will depend upon each plant's ability to handle any particular waste stream.
- 47. The use of cement kilns as a disposal operation not leading to resource recovery (i.e., the destruction or irreversible transformation of hazardous waste constituents), should be considered only if there are environmental benefits: for example, NOx reduction through flame cooling or when there is no other cost-effective and environmentally sound disposal option at the local level. Permit requirements should be set accordingly.
- 48. Where cement kilns are used for the destruction of hazardous waste constituents, alternative disposal routes need to be carefully assessed; strict environmental, health and safety standards adhered to; and the quality of the final product not impaired. In countries where there are no stringent requirements for the final product, application of BAT and BEP are considered even more important (UNEP, 2007).
- 49. As a result of the heterogeneous nature of waste, blending and mixing of different hazardous and non-hazardous waste streams may be required to guarantee a homogeneous feedstock that meets specifications for use in a cement kiln. Blending of hazardous wastes should not, however, be conducted with the aim of lowering the concentration of hazardous constituents to circumvent regulatory requirements. As a general principle, the mixing of wastes should be prevented from leading to the application of an unsuitable (non-environmentally sound) disposal operation (EIPPCB, 2006)3.

## 1. Hazardous wastes suitable for co-processing in cement kilns

50. A wide range of hazardous wastes are suitable for co-processing, but because cement kiln emissions are site-specific, there is no uniform answer to the type of waste that can be used in a specific plant. The selection of wastes is influenced by various factors. These include: the nature of the waste; its hazardous characteristics; available waste management operations; kiln operation; raw material and fuel compositions; waste feed points; exhaust gas cleaning process; resulting clinker quality; general environmental impacts; probability of formation and release of POPs; particular waste management considerations; regulatory compliance; and public and government acceptance (Van Oss and Padovani, 2003; GTZ/Holcim, 2006; UNEP, 2007; EIPPCB, 2010).

<sup>3</sup> In the European Union the requirements concerning the mixing of hazardous waste of the Directive 2008/98/EC apply.

51. The operator should develop a waste evaluation procedure to assess potential impacts on the health and safety of workers and the public, plant emissions, operations and product quality. Variables that should be considered when selecting waste include (WBCSD, 2005; UNEP, 2007):

#### (a) Kiln operation:

- (i) Alkali (sodium, potassium, etc.), sulphur and chloride content: Excessive inputs of these compounds may lead to build-up and blockages in the kiln system. Where these cannot be captured in the cement clinker or kiln dust, a bypass may be required to remove excess compounds from preheater/precalciner kiln systems. High alkali content may also limit recycling of CKD in the kiln itself;
- (ii) Heating (calorific) value: The key parameter for the energy provided to the process;
- (iii) Water content: Overall moisture content may affect productivity, efficiency and also increase energy consumption. The water content of waste needs to be considered in conjunction with that of conventional fuels and/or raw feed materials;
- (iv) Ash content: The ash content affects the chemical composition of the cement and may require an adjustment of the composition of the raw mix;
- (v) Exhaust gas flow rate and waste feed rate: Sufficient residence time is needed for the destruction of organics and to prevent incomplete combustion due to waste overcharging;
- (vi) Stability of operation (for example, duration and frequency of CO trips) and the waste's state (liquid, solid), preparation (shredded, milled) and homogeneity;

#### (b) Emissions:

- (i) Organic content: Organic constituents are associated with emissions of CO2 and may result in emissions of CO and other products of incomplete combustion (PICs) if waste is fed through unsuitable points or during unstable operating conditions:
- (ii) Chloride content: Chlorides may combine with alkalis to form fine, difficult to control particulate matter. In some cases, chlorides have combined with ammonia present in the limestone feed. This produces highly visible detached plumes of fine particulate with a high ammonium chloride content;
- (iii) Metals content: The non-volatile behaviour of most heavy metals allows most to pass straight through the kiln system and be incorporated into the clinker. Introduced volatile metals will partly be recycled internally by evaporation and condensation until equilibrium is reached, the other part being emitted in the exhaust gas. Thallium, mercury and their compounds are highly volatile as to a lesser extent are cadmium, lead, selenium and their compounds. The fact that dust control devices can only capture the particle-bound fraction of heavy metals and their compounds needs to be taken into account. Wood treated with preservatives containing copper, chromium and arsenic also requires special consideration with regard to the efficiency of the exhaust gas cleaning system. Mercury is a highly volatile metal, which, depending on the exhaust gas temperature is present in both particle-borne and vapour forms in the air pollution control equipment (EIPPCB, 2010);
- (iv) Alkali bypass exhaust gas can be released from either a separate exhaust stack or from the main kiln stack in systems equipped with an appropriate bypass. The same hazardous air pollutants are found in both the main and alkali bypass stacks. Where an alkali bypass system is installed, appropriate control of the exhaust to atmosphere also needs to be provided on the bypass exhaust, similar to that mandated for the main exhaust stack (UNEP, 2007);
- (v) High sulphur content in raw materials, fuel and waste may result in the release of SO<sub>2</sub>;
- (c) Clinker, cement and final product quality:
  - (i) High levels of phosphate may delay setting time;

- (ii) (High levels of fluorine will affect setting time and strength development;
- (iii) High levels chlorine, sulphur and alkali may affect overall product quality;
- (iv) Thallium and chromium content can adversely affect cement quality and may cause allergic reactions in sensitive users. Leaching of chromium from concrete debris may be more prevalent than leaching of other metals (Van der Sloot et al., 2008). Limestone, sand and clay contain chromium, making its content in cement both unavoidable and highly variable. The Norwegian National Institute of Occupational Health (Kjuus et al., 2003) reviewed several studies of chromate allergy, especially those involving construction workers. It found that the main sources of chromium in cement came from raw materials, refractory bricks in the kiln and chromium steel grinders. The relative contribution of these factors may vary depending on the chromium content of the raw materials and the manufacturing conditions. Minor sources include both conventional and alternative fuels (EIPPCB, 2010). Cement eczema can be caused by exposure to wet cement with a high pH, which induces irritant contact dermatitis and by an immunological reaction to chromium that elicits allergic contact dermatitis (Kjuus et al., 2003). Where there is a possibility of contact with the skin, cement and cement-containing preparations may not be used or placed on the market in the European Union, if they contain, when hydrated, more than 0.0002 per cent soluble chromium (VI) of the total dry weight of the cement.4 As the main chromate source is from the raw material, a reduction in chromium levels (VI) in cement requires that a reducing agent is added to the finished product. The main reducing agents used in Europe are ferrous sulphate and tin sulphate (EIPPCB, 2010).
- (v) Leachable trace elements: Heavy metals are present in all feed materials, conventional and otherwise. However under certain test conditions, leached concentrations from concrete of other metals besides chromium may approach drinking water standards (GTZ/Holcim, 2006).
- 52. Not all wastes are suitable for co-processing. Only waste of known composition, energy and mineral value is suitable for co-processing in cement kilns. Equally, plant-specific health and safety concerns need to be addressed and due consideration given to the waste management hierarchy. Co-processing should only be applied only if all tangible preconditions and requirements of environmental, health and safety, social, economic and operational criteria are fulfilled (UNEP, 2007).
- 53. Hazardous wastes that are, in principle, well-suited for co-processing in cement kilns include: tank bottom sludges, acid alkyl sludges, oil spills and acid tars from petroleum refining, natural gas purification and pyrolytic treatment of coal; waste machining oils; waste hydraulic oils and brake fluids; bilge oils; oil/water separator sludges, solids or emulsions; washing liquids and mother liquors, still bottoms and reaction residues from the manufacture, formulation, supply and use of basic organic chemicals, plastics, synthetic rubber, man-made fibres, organic dyes, pigments, organic pesticides and pharmaceuticals; waste ink; wastes from the photographic industry; tars and other carbon-containing wastes from anode manufacture (aluminium thermal metallurgy); wastes from metal degreasing and machinery maintenance; wastes from textile cleaning and degreasing of natural products; process wastes from the electronic industry (GTZ/Holcim, 2006).
- 54. The following wastes should not, in principle, be co-processed in cement kilns:
  - (a) Radioactive or nuclear waste;
  - (b) Electrical and electronic waste (e-waste);
  - (c) Whole batteries;
  - (d) Corrosive waste, including mineral acids;
  - (e) Explosives;
  - (f) Cyanide bearing waste;
  - (g) Asbestos-containing waste;

<sup>4</sup> Directive 2003/53/EC of the European Parliament and of the Council, of 18 June 2003, Amending for the 26th Time Council Directive 76/769/EEC Relating to Restrictions on the Marketing and Use of Certain Dangerous Substances and Preparations (Nonylphenol, Nonylphenol Ethoxylate and Cement).

- (h) Infectious medical waste;5
- (i) Chemical or biological weapons destined to destruction;
- (i) Waste consisting of, containing or contaminated with mercury;
- (k) Waste of unknown or unpredictable composition, including unsorted municipal waste.
- 55. Individual facilities may also exclude other wastes depending on local circumstances.
- 56. In general these wastes are not recommended because of health and safety concerns, potentially negative impacts on kiln operation, clinker quality and air emissions, and when a preferable alternative waste management option is available. Further details pertaining to the above-mentioned wastes may be found in GTZ/Holcim (2006).
- 57. Inputs of wastes containing or contaminated with mercury to the kiln should be avoided and kept to a minimum. As limiting the amount of mercury in the waste does not assure low mercury air emissions from the kiln, an emission limit value for mercury should also be in place.

#### 2. Waste recovery or disposal not leading to recovery in cement kilns

- 58. If selected waste streams with recoverable energy value meet specifications, they can be used as alternative fuels in a cement kiln to replace a portion of conventional fuels. Similarly, waste streams containing useful components such as calcium, silica, alumina and iron, e.g., waste tyres, can be used to replace raw materials such as clay, shale and limestone. Wastes meeting both sets of requirements may be suitable for processing for both energy and materials recovery.
- 59. Conversely, waste combustion in a cement kiln without any substitution, solely for the purpose of destruction or irreversible transformation of hazardous substances in wastes, should not be considered a recovery operation.6
- 60. To distinguish between operations that lead to resource recovery and those that do not, specific criteria may need to be developed to evaluate the contribution of the waste to the production process, outlined in figure I. Some approaches have been proposed that consider, for example, either the higher or the lower heating value of the waste to assess its energy value, and the material's chemical composition (ash, CaO or CaCO3, SiO2, Al2O3, Fe2O3, SO3, and/or water) to assess its mineral value (Zeevalkink, 1997; Koppejan and Zeevalkink, 2002; GTZ/Holcim, 2006). An example is provided in figure II.
- 61. Although for all practical purposes wastes without energy or mineral value should not be considered for co-processing, the high temperatures, long residence times and oxidizing conditions provided by cement kilns make it possible. At the request of national or local governments, kilns can be used for the purpose of the destruction or irreversible transformation of hazardous substances in particularly problematic waste streams, such as obsolete pesticide stocks. This, however, is an activity that falls outside the scope of co-processing and needs to be assessed on a case-by-case basis and agreed upon jointly by regulatory authorities and operators. Trial burns may need to be conducted to demonstrate that performance criteria are met.
- 62. It should be noted that cement kilns are primarily production processors for clinker and not all operating conditions are ideal for the destruction of hazardous substances. For example, cement kilns tend to operate at lower exhaust oxygen levels and more elevated carbon monoxide levels than well-operated incinerators. The thermal treatment of organic wastes requires high temperature, long residence time, the availability of adequate oxygen and sufficient mixing between the organic compounds and the oxygen. Good design and operation are thus critical to the use of cement kilns for

<sup>5</sup> Although lack of regulations (or their enforcement) governing health care waste management, particularly segregation at the source, will likely cause some facilities to not accept this type of waste based on health and safety concerns, process conditions in cement kilns would be appropriate to dispose of infectious wastes. In countries where occupational health and safety legislation so allows, such wastes may be co-processed in cement kilns.

<sup>6</sup> Under the Basel Convention the term "disposal" is used to refer to operations listed in both Annex IV.A (operations which do not lead to the possibility of resource recovery, recycling, reclamation, direct re-use or alternative uses) and Annex IV.B (operations which may lead to resource recovery). However, in some countries, disposal refers only to the operations specified in Annex IV A, that is to say, to such operations which do not lead to any form of recovery. The destruction of hazardous substances may be covered by operations R1 or D10 of Annex IV.

this application, otherwise situations can arise in cement kilns where wastes are not treated adequately if they are not introduced properly or available oxygen levels are too low. (UNEP, 2007).

Figure I

#### Hazardous waste acceptance decision process

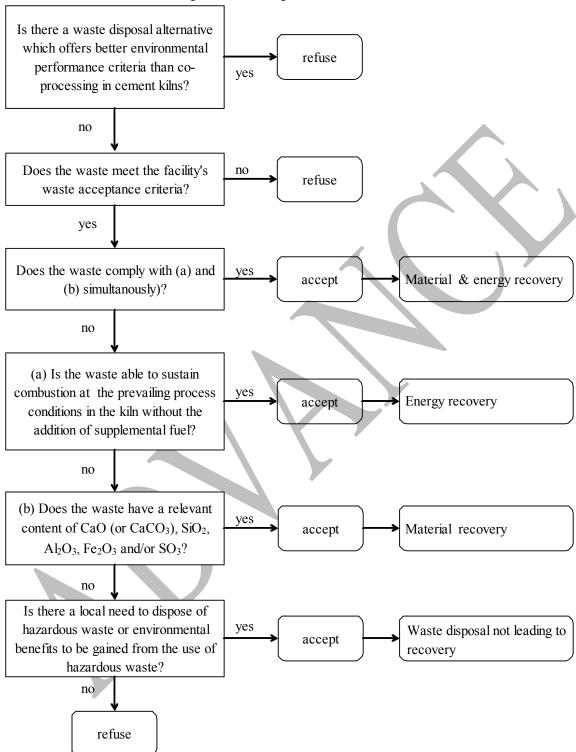
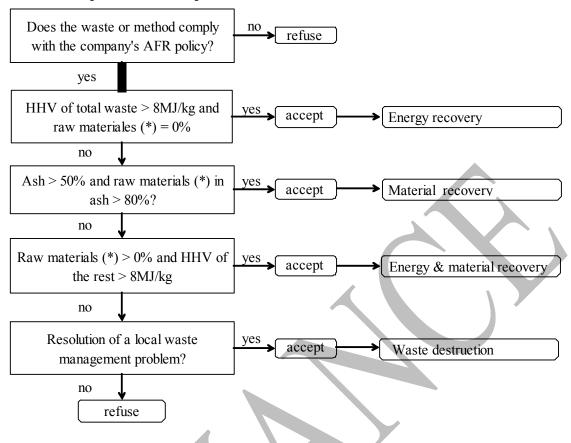


Figure II

Example of a waste acceptance decision chart



HHV: Higher heating (calorific) value AFR: Alternative fuels and raw materials (\*) CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>

Source: GTZ/Holcim (2006)

#### 3. Destruction efficiency of hazardous organic substances

- 63. Professionally supervised and independently verified trial burns should be conducted to demonstrate destruction of POP wastes. (Karstensen, 2008a). In advance, the operator should demonstrate to the satisfaction of the competent authorities that the baseline operation is properly controlled with safeguards in place against potential environmentally damaging abnormal operations. The requirements set out in table 2 should be thoroughly considered.
- 64. A trial burn is used to determine the facility's destruction and removal efficiency (DRE) or destruction efficiency (DE) to verify its ability to efficiently destroy POPs in an irreversible and environmentally sound manner. This involves the selection, sampling and analysis of a principal organic hazardous constituent (POHC) in the waste feed to determine its input and emission rates. A trial burn typically consists of a series of tests, one for each set of operating conditions in the facility. Three runs are normally performed for each test.
- 65. During the trial burn operating limits are established for maximum hazardous waste feed and maximum kiln production rate, parameters that may adversely affect the attainment of the demonstrated DRE or DE during routine operations (Karstensen, 2009b). Permit limits are established for these parameters subsequent to the trial burn.
- 66. The potential use of cement kilns to thermally destroy polychlorinated biphenyls (PCBs) has been investigated in many countries. The DREs determined from several trial burns indicate that well-designed and well-operated cement kilns are effective at destroying PCBs. A DRE of 99.9999 per cent is required by several jurisdictions for PCBs (for example, under the United States Toxic Substances Control Act, TSCA), which could be used as an indicative BAT standard (UNEP, 2007).
- 67. A facility should demonstrate its capability to destroy (combustion) or remove (settling in ductwork or air pollution control devices) at least 99.9999 per cent of targeted POPs. Moreover, a

PCDDs/PCDFs emission limit of 0.1 ng TEQ/Nm<sup>3; 7</sup> should be met under testing conditions (SBC, 2007). Existing emission limit values should also be met.

- 68. An alternative approach providing the same qualitative information to trial burns, under worst-case conditions, has been proposed by Karstensen (2009b). This requires a baseline emissions study with no hazardous waste fed to the kiln. A single test is then run to obtain destruction performance and pollutant emissions data while feeding hazardous waste into the kiln. Both tests are conducted under normal operating conditions, meeting an emissions limit for PCDDs/PCDFs of 0.1 ng TEQ/Nm³ and other regulatory requirements. This approach for performance verification, together with adequate safety arrangements, input control and operational procedures, is thought to secure the same level of environmental protection as current regulation in the European Union (GTZ/Holcim, 2006). This approach was used to demonstrate a DRE of 99.9999969 per cent for fenobucarb and 99.9999832 per cent for fipronil in a cement kiln in Viet Nam (Karstensen et al., 2006).
- 69. A compilation of performance verification and trial burns results is provided in annex I to the present guidelines.

## C. Quality assurance/quality control

- 70. A comprehensive programme for quality assurance (QA) and quality control (QC) should be applied. The aim is to ensure that the product meets standard specifications, plant operations are not negatively affected by the use of hazardous wastes, environmental protection and to reduce health and safety risks. QA is necessary for ensuring that all data and the decisions resulting from that data are technically sound, statistically valid, and properly documented.
- 71. A QA plan should be prepared to help ensure that the monitoring, sampling, and analytical data meet specific objectives for precision, accuracy, and completeness and to provide the framework for evaluating data quality. The plan should cover waste streams and product materials handled at the facility with detailed instructions for the following:
  - (a) Organization and responsibilities;
- (b) QA objectives for data measurement of precision, accuracy, completeness, representativeness, and comparability;
  - (c) Sampling procedures;
  - (d) Sample handling and custody;
  - (e) Analytical procedures;
  - (f) QC checks (blanks, spikes, replicates, etc.) and frequency;
  - (g) Instrument/equipment testing, inspection, or maintenance;
  - (h) Instrument/equipment calibration procedures and frequency;
  - (i) Data review, verification, validation, and reporting.
- 72. Adequate laboratory design, infrastructure, equipment, and instrumentation should be provided and maintained to ensure that all required analyses are completed in a timely manner. Periodic tests of the laboratory should be considered to evaluate and improve performance.
- 73. Safety and health should be taken into consideration when conducting sampling. Employees carrying out sampling require training for the hazards associated with waste, handling procedures, protective clothing and equipment. Those involved in sampling activities should be fully aware of applicable QA/QC procedures.
- 74. BAT for waste quality control in cement manufacturing processes is outlined by the EIPPCB (2010):
- (a) To apply QA systems to guarantee the characteristics of wastes and to analyse any waste that is to be used as raw material and/or fuel in a cement kiln for: maintenance of quality over time; physical criteria, for example, emissions formation, coarseness, reactivity, burnability, calorific value; chemical criteria, for example, chlorine, sulphur, alkali and phosphate content and relevant metals content;

<sup>7</sup> Dry basis, corrected to 11 percent O2, 101.3 kPa and 273.15 K.

- (b) To control the amount of relevant parameters for any waste that is to be used as raw material and/or fuel in a cement kiln, such as chlorine, relevant metals (for example, cadmium, mercury, thallium), sulphur, total halogen content;
  - (c) To apply QA systems for each waste load.
- 75. Internal audits should be carried out with a frequency that ensures QA/QC procedures are in use and that personnel conform to them. Independent third party audits should be conducted at least annually or as required to determine the effectiveness of the implemented quality system. Audit reports should be submitted to management with requirements to correct observed deficiencies.

## D. Health and safety aspects

- 76. Health and safety should be a conscious priority and integrated into all aspects of operations during hazardous waste management. Overall and specific personnel requirements, the chain of command, and individual roles and responsibilities, should be clearly established.
- 77. A health and safety programme should be designed to identify, evaluate, and control safety and health hazards, and provide for emergency response for hazardous waste operations. The content and extent of this programme should be proportionate to the types and degrees of hazards and risks associated with specific operations.
- 78. Adequate documentation and information on safe hazardous waste handling, operating procedures and contingency measures should be available. Through openness and transparency, facility management should ensure the workforce is fully informed about health and safety measures and standards. Easily understood safety and emergency instructions should be provided to employees and contractors in advance.
- 79. In the European Union, the BAT includes the appliance of hazardous waste safety management to the handling, storage, and the feeding of hazardous waste materials. For example, using a risk based approach according to the source and type of waste, for the labelling, checking, sampling and testing of waste to be handled. (EIPPCB, 2010).

#### 1. Hazard analysis

80. Hazards and potential exposures should be determined and appropriate controls should be in place to maintain employee health and safety. Hazards requiring the use of personal protective equipment (PPE) should be identified. Assessments such as job hazard analysis (JHA), job safety analysis (JSA), safety analysis reports (SAR), process hazard analysis (PHA), and job, task, and hazard analysis (JTHA), are recommended.

#### 2. Access and hazard control

- 81. To eliminate or control worker exposure to hazards, the following should be considered in order of preference:
- (a) Engineering controls to preclude worker exposure by removing or isolating the hazard. For example, ventilation or use of remotely operated material handling equipment;
- (b) Administrative controls to manage worker access to hazards and establish safe working procedures. For example, security measures to prevent unauthorized or unprotected access to hazardous wastes on-site;
- (c) PPE, when engineering or administrative controls are not feasible or do not totally eliminate the hazard.
- 82. These controls are designed to reduce and maintain employee exposure below national occupational exposure limit values. If these are not available, internationally recognized exposure levels should be considered.
- 83. Examples include: the Threshold Limit Value (TLV) occupational exposure guidelines by the American Conference of Governmental Industrial Hygienists (ACGIH); the Pocket Guide to Chemical Hazards by the United States National Institute for Occupational Health and Safety (NIOSH); Permissible Exposure Limits (PELs) by the Occupational Safety and Health Administration of the United States (OSHA); Indicative Occupational Exposure Limit Values (IOELVs) by European Union member states, or other similar sources.
- 84. For hazardous substances and health hazards for which there are no permissible or applicable exposure limits, the operators could use the published literature and material safety data sheets (MSDS) as a guide to determine an appropriate level of protection.

#### 3. Personal protective equipment

- 85. Employees, contractors and visitors to an installation should be provided with PPE where engineering control methods are not feasible to reduce exposure to permissible exposure limits. PPE should be selected to protect against any present or potential hazard and appropriate to the task-specific conditions and duration.
- 86. All personnel involved in hazardous waste operations should be fully aware of: equipment selection and use, maintenance and storage, decontamination and disposal, training and proper fit, donning and doffing procedures, inspection, in-use monitoring, programme evaluation, and equipment limitations.

#### 4. Training

- 87. Employees should be effectively trained to a level determined by their job function and responsibility. This should be carried out prior to them being permitted to engaging in hazardous waste operations that could expose them to hazardous substances, safety, or health hazards. Training activities should be adequately monitored and documented in terms of curriculum, duration, and participants.
- 88. The training should cover safety, health and other hazards present on the facility; use of personal protective equipment; work practices to minimize risks from hazards; safe use of engineering controls and equipment on the site; medical surveillance, including recognition of symptoms and signs that could indicate over exposure to hazards. Those engaged in hazardous emergency response should also be appropriately trained.

#### 5. Medical surveillance

- 89. A medical monitoring programme should be implemented to assess and monitor employee health both prior and during employment. An effective programme should consider the following components as a minimum:
- (a) Pre-employment screening, to determine fitness-for-duty, including the ability to work while wearing PPE, and provide baseline data for future exposures;
- (b) Periodic medical monitoring examinations (the content and frequency of which depend on the nature of the work and exposure), to determine biological trends that may mark early signs of chronic adverse health effects;
  - (c) Provisions for emergency and acute non-emergency treatments.

#### 6. Emergency response

- 90. Emergency plans and procedures should be established for the protection of the workforce and public before hazardous waste operations begin. An Emergency Response Plan, ensuring appropriate measures to handle possible on-site emergencies and coordinate off-site response, should be in place. As a minimum, this plan should address the following:
  - (a) Pre-emergency planning and coordination with outside emergency responders;
  - (b) Personnel roles, lines of authority, training and communication procedures;
  - (e) Emergency recognition and prevention procedures;
  - (d) Safe distances and places of refuge;
  - (e) Site security and control procedures;
  - (f) Evacuation routes and procedures;
- (g) Site mapping highlighting hazardous areas, site terrain, site accessibility and off-site populations or environments at potential risk;
  - (h) Decontamination procedures;
  - (i) Emergency medical treatment and first aid procedures;
  - (j) Personal protective and emergency equipment at the facility;
  - (k) Emergency alerting and response procedures:
  - (l) Documenting and reporting to local authorities;
  - (m) Critique of response and follow-up procedures.

- 91. Emergency equipment, such as fire extinguishers, self-contained breathing apparatus, sorbents and spill kits, and shower/eye wash stations should be located in the immediate vicinity of hazardous waste storage and processing areas.
- 92. The Plan procedures should be rehearsed regularly using drills and mock situations, and reviewed periodically in response to new or changing conditions or information.
- 93. Arrangements should be made to familiarize local authorities and emergency responders with the layout of the facility; properties of hazardous waste handled at the facility and associated hazards; places where facility personnel would normally be working; facility entrances and possible evacuation routes. Arrangements agreed to by local authorities, hospitals and emergency response teams should be described in the Emergency Response Plan.

#### E. Communications and stakeholder involvement

- 94. Stakeholders are those who see themselves as potentially affected by the operations of a facility. These can be individuals and groups on a local, national, or international scale and include neighbours, community organizations, employees, trade unions, government agencies, the media, non-governmental organizations, contractors, suppliers and investors.
- 95. Public communication is the provision of information through media sources, including brochures, websites, newspapers, radio and television. Stakeholder involvement is concerned with community members and others with an interest in the facility, through public meetings, presentations, advisory committees, and personal approaches. Both should form part of the normal operations of a plant.
- 96. Facilities should have clear objectives for working with stakeholders. This includes a realistic timescale for engagement, committing necessary resources and a willingness to find mutually beneficial outcomes. Advice for the design and development of a communications and stakeholder involvement plan is provided by United States EPA (1996), Hund et al. (2002), and The Environment Council (2007), among others.
- 97. Operators and regulatory authorities should be prepared to address public concerns over possible impacts of co-processing and strive to establish efficient communication methods to explain the activities. Operators planning on using hazardous waste should provide all necessary information to allow stakeholders to understand the use of the wastes in the cement kiln while illustrating the measures that would be implemented to avoid adverse impacts.

## IV. Environmentally sound waste acceptance and pre-processing

## A. Introduction

- 98. Due to the heterogeneity of waste, pre-processing is required to produce a relatively uniform waste stream for co-processing in cement kilns. This waste stream should comply with the technical and administrative requirements of cement manufacture and guarantee that environmental standards are met8. In some cases, for example used oil or tyres, wastes may be used 'as-delivered' and without pre-processing.
- 99. Attention should be paid to the selection of suitable waste materials, whether they are collected directly from the generators or through intermediaries. Operators should ensure that only hazardous waste originating from trustworthy parties is accepted and deliveries of unsuitable waste refused.
- 100. Consideration should be given to the integrity of all participants throughout the supply chain. For example, only qualified, authorized and licensed transport companies should be used in order to avoid accidents and incidents due to the incompatibility of poorly labelled or poorly characterised wastes being mixed or stored together.
- 101. These recommendations only provide general indications. Specific handling requirements should be identified on the basis of the chemical and biological characteristics of individual waste streams, environmental and health effects, the safety of personnel, and compliance with permitting requirements and local regulations.

<sup>8</sup> Pre-processing should be carried out because it is a technical requirement from the kiln operator to guarantee a homogeneous and stable feedstock and not to circumvent waste acceptance procedures.

## B. Waste acceptance

- 102. Prior knowledge of wastes is necessary to ensure that the waste falls within the requirements of the facility's permit and will not adversely affect the process. For instance, to avoid operating problems within the kiln, the impact of hazardous waste on the total input of circulating volatile elements, such as chlorine, sulphur or alkalis, requires careful assessment prior to acceptance. Specific acceptance criteria for these components should be set by each facility based on the process type and on the specific kiln conditions.
- 103. Generators of hazardous waste should in most circumstances know the composition, nature and problems associated with their waste, ensuring that all relevant information is passed on to those involved in its subsequent management.
- 104. Hazardous and non hazardous waste acceptance comprises two stages: pre-acceptance (or screening) and on-site acceptance. Pre-acceptance involves the provision of information and representative samples of the waste to allow operators to determine suitability before arrangements are in place for acceptance. The second stage concerns procedures when the waste arrives at the facility to confirm previously approved characteristics.
- 105. Failure to adequately screen waste samples prior to acceptance and a confirmation of its composition on arrival at the installation may lead to subsequent problems. Inappropriate storage, mixing of incompatible substances, and accumulation of wastes could occur.

#### 1. Pre-acceptance

- 106. A pre-acceptance, or pre-shipment screening, protocol should ensure that only properly and safely handled hazardous waste streams are approved for shipment to the facility. Such protocol is necessary to:
  - (a) Ensure regulatory compliance by screening out unsuitable wastes;
- (b) Confirm the details relating to composition, and identify verification parameters that can be used to test waste arriving at the facility;
- (c) Identify any substances within the waste that may affect its processing, or react with other reagents;
  - (d) Accurately define the range of hazards exhibited by the waste.
- 107. The operator should obtain information on the nature of the process producing the waste, including its variability. Other required descriptions include: composition (chemicals present and individual concentrations); handling requirements and associated hazards; the quantity and the form of waste (solid, liquid, sludge etc); sample storage and preservation techniques. Ideally, information should be provided by the waste generators. Alternatively a system for the verification of the information provided by any intermediaries should be considered.
- 108. Systems for the provision and analysis of waste representative samples should be in place. The waste sample should be taken by a competent technician and the analysis carried out by a laboratory, preferably accredited with robust QA/QC methods and record keeping and a chain-of-custody procedure should be considered. The operator should carry out a comprehensive characterisation (profiling) and testing with regard to the planned processing for each new waste. No waste should be accepted without sampling and testing being carried out. The exception is unused, outdated or off-specification uncontaminated products that have appropriate MSDS or product data sheets.
- 109. A Waste Analysis Plan (WAP) should be prepared and maintained to document procedures used to obtain a representative waste sample and to conduct a detailed chemical and physical analysis. A WAP should address measures used to identify potentially reactive and incompatible wastes. It should include testing of a representative sample to qualify the waste for use at the facility (pre-acceptance) and to verify its constituents (acceptance). Further testing of samples taken during or after waste pre-processing or blending should be used to verify the quality of the resultant stream.
- 110. Operators should ensure that the technical appraisal is carried out by qualified, experienced staff who understands the capabilities of the facility.

<sup>9</sup> The United States EPA document, "A Method of Determining the Compatibility of Hazardous Wastes" (EPA-600/2-80-076), contains procedures to evaluate qualitatively the compatibility of various categories of wastes.

111. Records of pre-acceptance should be maintained at the facility for cross-referencing and verification at the waste acceptance stage. Information should be recorded and referenced, available at all times, regularly reviewed and kept up to date with any changes to the waste stream.

#### 2. On-site acceptance

- 112. On-site verification and testing should confirm waste characteristics with the pre-acceptance information. Acceptance procedures should address:
- (a) Pre-approved wastes arriving on-site, such as a pre-booking system to ensure that sufficient capacity is available
  - (b) Traffic control;
  - (c) Check for documents arriving with the load;
  - (d) Load inspection, sampling and testing;
  - (e) Rejection of wastes and the discrepancy reporting procedures;
  - (f) Record keeping;
  - (g) Periodic review of pre-acceptance information.
- 113. Wastes should not be accepted without detailed written information identifying the source, composition and hazard levels.
- 114. Where facilities provide an emergency service such as the removal of spillages or fly-tipped hazardous wastes, there may be situations where the operator is unable to adhere to established preacceptance and/or acceptance procedures. In such instances, the operator should communicate the occurrence to the competent authorities immediately.

#### (a) Arrival

- 115. If sufficient storage capacity exists and the site is adequately manned, suitably qualified and trained personnel should supervise the receiving of hazardous wastes. All wastes received should be treated as unknown and hazardous until compliance with specifications has been positively verified.
- 116. A suitable description should accompany hazardous waste delivery including: name and address of the generator; name and address of the transporter; waste classification and description; volume and weight; hazards of the waste such as, flammability, reactivity, toxicity or corrosivity.
- 117. Documentation accompanying the shipment should be reviewed and approved, including the hazardous waste manifest, if applicable. Any discrepancies should be resolved before the waste is accepted. If they cannot be resolved, the waste should be rejected and sent back to the original generator, or at its request, to an alternate facility.
- 118. Where possible, waste loads should be visually inspected. All containers should be clearly labelled in accordance with applicable regulations for the transport of dangerous goods and checked to confirm quantities against accompanying documentation. They should be equipped with well-fitting lids, caps and valves secure and in place and inspected for leaks, holes, and rust. Any damaged, corroded or unlabelled container or drum should be classified as 'non-conforming' and dealt with appropriately.
- 119. All incoming loads should be weighed, unless alternative reliable volumetric systems linked to specific gravity data are available.

#### (b) Inspection

- 120. Wastes should only be accepted at the facility after thorough inspection. Reliance solely on supplied written information should not be acceptable. Physical verification and analytical confirmation should be undertaken to ensure the waste meets permit specifications and regulatory requirements. All wastes, whether for processing or storage, should be sampled and undergo verification and testing, according to the frequency and protocol defined in the WAP, except for unused, outdated, off-specification or uncontaminated products.
- 121. On-site verification and testing should take place to confirm:
  - (a) The identity and description of the waste;
  - (b) Consistency with pre-acceptance information;
  - (c) Compliance with the facility permit.

- 122. Techniques for inspection vary from simple visual assessment to full chemical analysis. The extent of the procedures adopted will depend upon waste chemical and physical composition and variation; known difficulties with certain waste types or of a certain origin; specific sensitivities of the installation concerned (for example, certain substances known to cause operational difficulties); and the existence or absence of a quality controlled specification for the waste, among others. (Karstensen, 2008a)
- 123. The facility should have a designated sampling or reception area where containerised waste is unloaded if adequate space is available and temporarily stored for further sampling and sample analysis. Wastes should be segregated immediately to remove possible hazards due to incompatibility. Sampling should ideally take place within 24 hours of unloading. During this period, hazardous wastes should not be bulked, blended or otherwise mixed. Bulk wastes should be inspected and accepted for processing prior to unloading.
- 124. Sampling should comply with specific national legislation, where it exists, or with international standards. Sampling should be supervised by laboratory staff and in those countries where regulations do not exist, qualified staff should be appointed. Sampling should include well-established procedures such as those developed by the American Society for Testing and Materials (ASTM), the European Committee for Standardization (CEN), and the United States Environmental Protection Agency (EPA). A record of the sampling regime for each load and justification for the selected option should be maintained.
- 125. Samples should be analysed by a laboratory with a robust QA/QC programme, including but not limited to suitable record keeping and independent assessments. Analysis should be carried out at a timescale required by facility procedures. In the case of hazardous wastes this often requires the laboratory to be on-site.
- 126. Typically, waste should be sampled and analysed for a few key chemical and physical parameters (fingerprint analysis) to substantiate the waste composition designated on the accompanying manifest or other documents. The selection of key parameters must be based on sufficient waste profile knowledge and testing data to ensure accurate representation. When selecting fingerprint parameters, consideration should be given to those that: identify unpermitted wastes; determine suitability within the facility's operational acceptance limits; identify potential reactivity or incompatibility; indicate any changes in composition that had occurred during transportation or storage. Should fingerprint testing results of a given waste stream fall outside the established tolerance limits, the waste may be re-evaluated for possible acceptance to prevent the unnecessary movement of waste back and forth between the generator and the installation. Re-evaluation should consider facility conditions for storage and processing; additional parameter analysis deemed appropriate by the operator and established in the WAP; permit requirements.
- 127. The inspection scheme may include: assessment of combustion parameters; blending tests on liquid wastes prior to storage; control of flashpoint; and screening of waste input for elemental composition, for example by ICP, XRF and/or other appropriate techniques, in accordance to waste types and characteristics, and the facility waste acceptance criteria. (Karstensen, 2008a)
- 128. Wastes should be moved to the storage area only after acceptance. Should the inspection or analysis indicate a failure to meet the acceptance criteria, including damaged or unlabelled drums, such loads should be stored in a quarantine area, allocated for non-conforming waste storage, and dealt with appropriately.
- 129. All areas where hazardous waste is handled should have an impervious surface with a sealed drainage system. Attention should be given to ensuring that incompatible substances do not come into contact resulting from spills from sampling, for example, within a sump serving the sampling point. Absorbents should be available.
- 130. In accordance with national legislation and practice, suitable provisions should be made to verify that wastes received are not radioactive, such as the use of plastic scintillation detectors.
- 131. After acceptance, containerised hazardous waste should be labelled with the arrival date and primary hazard class. Where containers are bulked, the earliest arrival date of the bulked wastes should be indicated on the bulk container. Each container should be given a unique reference number for inplant tracking.

#### 3. Non-conforming waste

132. The operator should have clear and unambiguous criteria for the rejection of wastes, including wastes that fail to meet the acceptance criteria, and damaged, corroded or unlabelled drums. A written

procedure for tracking and reporting such non-conformance should include notification to the customer or waste generator and competent authorities.

- 133. The operator should also have a clear and unambiguous policy for the subsequent storage, including a maximum storage volume, and disposal of rejected wastes. This policy should achieve the following:
  - (a) Identify the hazards posed by the rejected wastes;
- (b) Label rejected wastes with all information necessary to allow proper storage and segregation arrangements to be put in place;
- (c) Segregate and store rejected wastes safely pending removal within no more than five working days, where possible.
- 134. Wastes not fulfilling the acceptance criteria of the plant should be sent back to the waste generator, unless an agreement is reached with the generator to ship the rejected waste to an alternative authorised destination.

#### 4. In-plant tracking system

- 135. An internal wastes tracking system and stock control procedure should be in place, starting at the pre-acceptance stage, to guarantee the traceability of waste processing and enabling the operator to:
  - (a) Prepare the most appropriate waste blend;
  - (b) Prevent unwanted or unexpected reactions;
  - (c) Ensure that the emissions are either prevented or reduced;
  - (d) Manage wastes throughput.
- 136. The tracking system, which may be a paper-based, electronic, or a combination of both), should trace the waste during its acceptance, storage, processing and removal off-site. At any time, the operator should be able to identify the location of a specific waste on the facility and the length of time it has been there. Records should be held in an area removed from hazardous activities to ensure their accessibility during any emergency.
- 137. Once a waste has entered bulk storage or a treatment process, tracking individual wastes will not be feasible. However, records should be maintained to ensure sufficient knowledge is available as to what wastes have entered a particular storage facility. For example, to avoid incompatibility with incoming wastes, residues building up within a vessel between de-sludging operations should be tracked.
- 138. For bulk liquid wastes stock control should involve maintaining a record of the route through the process. Waste in drums should be individually labelled to record the location and duration of storage.
- 139. The in-plant waste tracking system should hold a complete record generated during preacceptance, acceptance, storage, processing and removal off-site. Records should be kept up to date to reflect deliveries, on-site treatment and dispatches. The tracking system should operate as a waste inventory, stock control system and include as a minimum:
  - (a) A unique reference number;
  - (b) Details of the waste generator and intermediate holders;
  - (c) Date of arrival on-site;
  - (d) Pre-acceptance and acceptance analysis results;
  - (e) Container type and size;
- (f) Nature and quantity of wastes held on-site, including identification of associated hazards;
  - (g) Details on where the waste is physically located;
- (h) Identification of staff who have taken any decisions on acceptance or rejection of wastes.
- 140. The system adopted should be structured to report on:
  - (a) Total quantity of waste present on-site at any one time, in appropriate units;

- (b) Breakdown of waste quantities being stored pending on-site processing;
- (c) Breakdown of waste quantities on-site for storage only, that is, awaiting transfer;
- (d) Breakdown of waste quantities by hazard classification;
- (e) Indication of where the waste is located relative to a site plan;
- (f) Comparison of the quantity on-site against total permitted;
- (g) Comparison of time the waste has been on-site against permitted limit.

#### C. Waste storage and handling

- 141. After deciding the waste's suitability, the operator should have systems and procedures in place for transfer to appropriate storage safely.
- 142. Considerations for waste storage on the installation should include:
  - (a) Location of storage areas;
  - (b) Storage area infrastructure;
  - (c) Condition of tanks, drums, vessels and other containers;
  - (d) Stock control;
  - (e) Segregated storage;
  - (f) Site security;
  - (g) Fire risk.
- 143. Useful information regarding storage of waste can also be found in the BREF for waste treatment industries (EIPPCB, 2006).

#### 1. Design considerations

- 144. Transfer and storage areas should be designed to handle accidental spills. This may require that:
- (a) To prevent spills from spreading or seeping into the soil, storage areas should have adequate boundaries and be adequately sealed, impermeable and resistant to the stored waste materials;
- (b) All spills should be collected, placed in a suitable container, and stored for disposal in the kiln;
  - (c) If a spill occurs, incompatible wastes should be prevented from mixing;
- (d) All connections between tanks should be capable of being closed by valves. Overflow pipes should be directed to a contained drainage system such as a bounded area or another vessel;
  - (e) Leak free equipment and fittings should be installed whenever possible;
  - (f) Measures to detect leaks and appropriate corrective action should be provided;
- (g) Contaminated runoff should be prevented from entering storm drains and watercourses. Any runoff should be collected and stored for disposal in the kiln;
  - (h) Adequate alarms for abnormal conditions should be provided.
- 145. Storage design should be appropriate to maintain waste quality for the complete storage period. Segregated storage should be in place to prevent incidents from incompatible wastes and as a means of preventing escalation should an incident occur. Individual storage requirements on a particular installation will be dependent on a full assessment of risk.
- 146. Within the facility, specific storage area characteristics should reflect the properties of the waste that poses the greatest risk that can be accepted. In general, the storage criteria should also take into account the unknown nature and composition of wastes, as this gives rise to additional risks and uncertainties. In many cases, this uncertainty means that higher specification storage systems are applied for wastes than for well-characterised raw materials.
- 147. Containerised wastes should be stored under cover, protected from heat, direct sunlight and rain, unless the waste is known to be unaffected by such ambient conditions.

- 148. For containerised wastes, the design should be such to prevent accumulation of hazardous wastes beyond the allowable storage timescale. For liquid wastes, mixing or agitation to prevent settling of solids should be considered. It may be necessary to homogenise tank contents with mechanical or hydraulic agitators. Depending on the waste characteristics, some tanks may need to be heated and insulated.
- 149. The construction, material selection and design of equipment, such as tanks, pipelines, valves, and seals should be appropriate for the characteristics of the waste. They should be sufficiently corrosion proof, and offer the option of cleaning and sampling.
- 150. Adequate ventilation should be provided in consideration to applicable work exposure guidelines. Periodic monitoring should be considered for open stored wastes that may emit VOC.
- 151. A fire protection system approved by local authorities, for example, a local fire department, should be in place. Automatic fire detection systems should be used in waste storage areas as well as for fabric filters and electrostatic precipitators (ESP), electrical and control rooms, and other identified risk areas. Continuous, automatic temperature measurement of the surface of wastes in the storage pits can be used to trigger an acoustic alarm to indicate temperature variations.
- 152. Automatic fire suppression systems should be used when storing flammable liquid waste and in other risk areas. Foam and carbon dioxide control systems provide advantages in some circumstances, for example, for the storage of flammable liquids. Water systems with monitors, water cannons with the option to use water or foam, or dry powder systems should be used, as appropriate, depending on the nature of the hazards on site.

#### 2. Operational considerations

- 153. Written procedures and instructions for the unloading, handling, and storage of wastes on-site should be in place. It should be ensured that chemically incompatible wastes are segregated. Compliance should be audited regularly.
- 154. To avoid the need for additional handling and transfer hazardous wastes should be stored in the same containers (drums) that were used for delivery.
- 155. Designated routes for vehicles carrying specific hazardous wastes should be clearly identified within the facility. On-site transportation should minimize risk to the health and safety of employees, the public and the environment. The operator should ensure that vehicles are fit for purpose with respect to compliance with relevant regulations.
- 156. All loads should be properly identified, segregated according to compatibility (so that any potential spills do not create chemical safety hazards), and secured to prevent sliding or shifting during transport. Personnel should be directed and trained to use equipment only as intended, and not to exceed the rated capacity of containers, vehicles, and other equipment.
- 157. Appropriate signage indicating the nature of hazardous wastes should be in place at storage, stockpiling, and tank locations.
- 158. Containers should be kept in good condition, free of dents, not leaking or bulging, and closed not in use. Container storage areas should have at least a weekly inspection.
- 159. Maintenance work should be authorized by plant management, and carried out after the area has been checked by a supervisor and all necessary precautions have been taken. Special procedures, instructions, and training should be in place for routine operations such as:
  - (a) Working at heights, including proper tie-off practices and use of safety harnesses;
- (b) Confined space entry where air quality, explosive mixtures, dust, or other hazards may be present;
- (c) Electrical lock-out, to prevent accidental reactivation of electrical equipment undergoing maintenance;
  - (d) 'Hot works' (welding, cutting, etc.) in areas that may contain flammable materials.
- 160. Safety measures that should be considered include:
  - (a) Placing of uncontrolled combustible materials in storage areas should be avoided;
- (b) Where there is a risk that has not been avoided or controlled, standard safety signs and information signs should be in place;

- (c) Emergency showers and eye wash stations should be provided within the work area for immediate emergency use following exposure to hazardous wastes. Consideration should be given to the possible need for multiple emergency shower installations, based upon access distance, and the possibility that more than one person may be affected at the same time;
  - (d) Adequate alarms should be provided to alert all personnel about emergency situations;
- (e) On site communication equipment should be maintained so that in case of a fire, the control room and the local fire department can be contacted immediately;
- (f) Electrical equipment should be earthed and have appropriate anti-static devices in place.

## D. Waste pre-processing

- 161. So as not to detract from normal kiln operation, product quality, or the site's usual environmental performance, wastes used in cement kilns should be homogenous, with compatible particle size, stable chemical composition and heat content. For optimum operation, kilns require very uniform waste material flows in terms of quality and quantity. For certain types of wastes, this can only be achieved by pre-processing.
- 162. Pre-processing includes drying, shredding, grinding or mixing depending on the type of waste. It is usually carried out in a purpose-made facility, which may be located outside or inside the cement plant.
- 163. Liquid waste fuels are normally prepared by blending different products with suitable calorific values and chemistry, such as spent solvents or used oil. Only simple pre-treatment is usually necessary, such as the removal of bottoms, sediments and water. In some cases, for example machining oil/emulsion, chemical processes are necessary to remove metallic pollutants and additives. The extent of solid waste processing, such as sorting, crushing, or pelletizing, depends on the specific application.

#### 1. Design considerations

- 164. Facility layout should be carefully considered to ensure access for day-to-day operations, emergency escape routes, and maintainability of the plant and equipment.
- 165. Recognized standards should be applied to the design of installations and equipment. Any modifications should be documented.
- 166. Health and safety assessments should be undertaken on operations to ensure equipment safety and to minimize risks of endangering people or installations, or damaging the environment. Appropriate procedures should be used to assess risks or hazards for each stage of the design process. Only competent and qualified personnel should undertake or oversee such hazard and operating studies.

#### 2. Operational considerations

- 167. Although mixing and homogenisation of wastes can improve feeding and combustion behaviour, it can involve risks and should be carried out according to a prescribed preparation.
- 168. Techniques used for waste pre-processing and mixing are wide ranging, and may include:
- (a) Mixing and homogenising of liquid wastes to meet input requirements, for example, viscosity, composition and/or heat content;
  - (b) Shredding, crushing, and shearing of packaged wastes and bulky combustible wastes;
  - (c) Mixing of wastes in a storage pit or similar enclosure using a grab or other machine.
- 169. Crane operators should be capable of identifying potentially problematic loads, for example, baled wastes and discrete items that cannot be mixed or may cause loading and feeding problems. These can then be removed, shredded or directly blended (as appropriate) with other wastes.
- 170. General tidiness and cleanliness should be applied to enhance working environment and to allow potential operational problems to be identified in advance. The main elements are:
  - (a) Systems to identify, locate and store wastes received according to their risks;
  - (b) The prevention of dust emissions from operating equipment;

- (c) Effective wastewater management;
- (d) Effective preventive maintenance.

## E. Pre-processing plant closure/decommissioning

- 171. Closure is the period directly after the facility stops normal operations. During this period the facility stops accepting hazardous waste; completes storage and processing of any wastes left on site; and disposes or decontaminates equipment, structures, and soils, restoring the site, insofar as possible, to its original condition or in keeping with the intended land use. Planning for decommissioning of the facility should be undertaken during the initial stages of the overall project. By integrating decommissioning requirements into the facility design at the outset, the site development plan should be compatible with the proper closure requirements when the operation of the facility has ended.
- 172. Operators should be required to properly close the facility in a manner that minimizes the further need for maintenance, and prevents the escape of any hazardous contaminants to the environment. To ensure this, a closure plan should be prepared identifying the steps necessary to partially or completely close the facility, including:
  - (a) Procedures for handling removed inventory;
  - (b) Procedures for decontamination and/or disposal;
- (c) Procedures to confirm effectiveness of decontamination, demolition and excavation, including procedures for performing sample collection and analysis;
- (d) Health and safety plan addressing all health and safety concerns pertinent to closure activities;
- (e) Security system to prevent unauthorized access to the areas affected by closure activities.
- 173. To prevent a facility from ceasing operations and failing to provide for the potentially costly closure requirements, operators should be required to demonstrate that they have the financial resources to properly conduct closure in a manner that protects both human health and the environment.
- 174. To minimise decommissioning problems and associated environmental impacts, it is recommended for existing installations, where potential problems are identified, to put in place a programme of design improvements (EIPPCB, 2006). These design improvements should ensure that underground tanks and piping are avoided. If replacement is not possible operators should provide secondary containment or develop a suitable monitoring programme. A procedure for the draining and cleaning out of vessels and piping prior to dismantlement, among others, should also be provided

### F. Other environmental aspects

#### 1. Volatile organic compounds, odours and dust

- 175. Emissions to air from waste pre-processing will depend on the types of wastes treated and the processes used. Emission monitoring and reporting should be performed according to operating permits and applicable regulations.
- 176. Abatement techniques should be in place as required and countermeasures for noise and odours considered. Dust is usually reduced by bag filters while VOC emission control technologies, if needed, may include carbon adsorption, thermal or biological treatments, among others.
- 177. In the European Union, BAT is to apply the following techniques to prevent or control the emissions of dust, odours and VOC in the waste treatment sector as a whole: restrict the use of open topped tanks, vessels and pits; use an enclosed system with extraction to suitable abatement plant; apply a suitably sized extraction system; correctly operate and maintain the abatement equipment; have leak detection and repair procedures in place; and reduce air emissions by using a suitable combination of preventive and/or abatement techniques (EIPPCB, 2006).

#### 2. Drums and ferrous metals

178. Empty drums and ferrous metals removed by magnetic separators should be disposed of in an environmentally sound manner. Scrap metal not containing any contaminants to an extent to render it hazardous can be recycled for steelmaking. Empty waste drums in good condition can be sent to authorised drum washers/recyclers.

#### 3. Wastewater

- 179. Discharges of wastewater to surface water should not result in contaminant concentrations in excess of local ambient water quality criteria, or in their absence, other recognized ambient water quality criteria. Receiving water use and assimilative capacity, taking other sources of discharges to the receiving water into consideration, should also influence the acceptable pollution loadings and effluent discharge quality.
- 180. Discharges into public or private wastewater treatment systems should meet the pre-treatment and monitoring requirements of that sewer treatment system. It should not interfere, directly or indirectly, with the operation and maintenance of the collection and treatment systems, or pose a risk to worker health and safety, or adversely impact characteristics of residuals from wastewater treatment operations.
- 181. In the European Union, BAT is to apply the following techniques to wastewater management in the waste treatment sector as a whole: reduce the water use and the contamination of water; avoid the effluent by-passing the treatment plant systems; collect spillages, drum washings, etc.; segregate the water collecting systems; have a concrete base in all the treatment areas; maximise the reuse of treated wastewaters; conduct daily checks on the effluent management system; carry out the appropriate treatment technique for each type of wastewater; achieve adequate water emission values before discharge by applying a suitable combination of techniques (EIPPCB, 2006).

## G. Emissions monitoring and reporting

- 182. Emissions and air quality monitoring programmes provide information that can be used to assess the effectiveness of relevant management strategies. A systematic planning process is recommended to ensure that data collected are adequate for the intended purposes and to avoid collecting data that are unnecessary. A monitoring programme for air quality should consider baseline monitoring to assess background levels of key pollutants both at and in the vicinity of the facility.
- 183. When wastewater is discharged, a monitoring programme, with adequate resources and management overview, for wastewater and water quality should be developed and implemented to meet set monitoring objectives.
- 184. The parameters selected for monitoring should be indicative of the pollutants of concern from the process, and should include parameters that are regulated under compliance requirements. Monitoring programmes should apply national or international methods for sample collection and analysis, such as those published by the International Organization for Standardization (ISO), CEN or the United States EPA. Sampling should be carried out or supervised by trained individuals. Those permitted or certified for this role should conduct the analysis. Sampling and analysis QA/QC plans should be applied and documented to ensure that data quality is adequate for the intended data use. Monitoring reports should include QA/QC documentation.
- 185. More useful information regarding monitoring principles can be found in the European Commission's Reference Document on the General Principles of Monitoring, which presents the results of an exchange of information carried out under Directive 2008/1/EC between European Union Member States and the industries concerned (EIPPCB, 2003). Good practice for reporting monitoring results is described in section 4.4.4 of the present guidelines.

## V. Environmentally sound co-processing of hazardous waste in cement kilns

#### A. Introduction

- 186. For optimal performance (co-processing without additional emissions) alternative fuels and raw materials should be fed to the cement kiln through appropriate feed points, in adequate proportions and with proper waste quality and emission control systems.
- 187. Co-processing has the following characteristics during the production process (GTZ/Holcim, 2006):
- (a) The alkaline conditions and the intensive mixing favour the absorption of volatile components from the gas phase. This internal gas cleaning results in low emissions of components such as SO2, HCl, and most of the heavy metals, with the exception of mercury, cadmium and thallium;
- (b) The clinker reactions at 1450°C allow the chemical binding of metals and the incorporation of ashes to the clinker;

(c) The direct substitution of primary fuel by high calorific waste material causes a higher efficiency on energy recovery in comparison to other 'waste to energy' technologies.

### **B.** Operational requirements

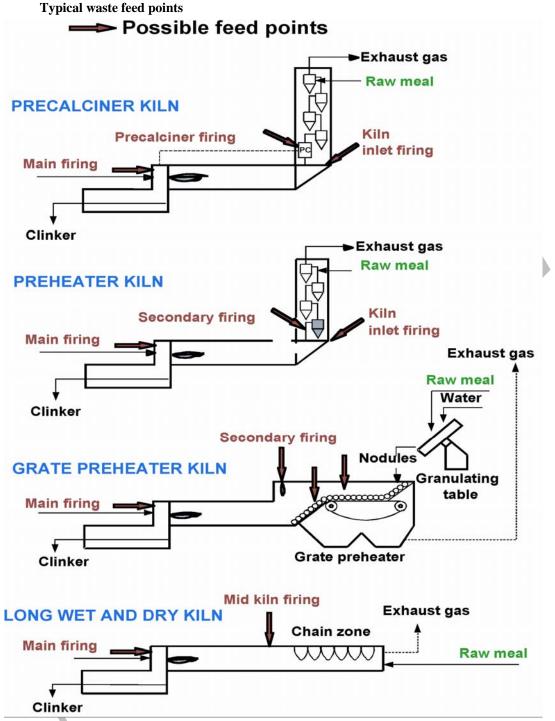
188. Safe and responsible co-processing requires careful selection of the feed points in the kiln system as well as comprehensive operational control relating to the specific characteristics and volumes of the waste material.

#### 1. Feed point selection

- 189. Adequate feed points should be selected according to relevant characteristics of the waste, including physical, chemical, and toxicological (see figure III). Different feed points can be used, most commonly waste is introduced via:
  - (a) The main burner at the rotary kiln outlet end;
  - (b) A feed chute at the transition chamber at the rotary kiln inlet end (for lump fuel);
  - (c) Secondary burners to the riser duct;
  - (d) Precalciner burners to the precalciner;
  - (e) A feed chute to the precalciner (for lump fuel);
  - (f) A mid kiln valve in the case of long wet and dry kilns (for lump fuel).



Figure III



- 190. Liquid wastes are typically injected into the hot end of the kiln. Solid wastes may be introduced into the calcining zone at some facilities. This is mid-kiln for long kilns, and onto the feed shelf in the high-temperature section for preheater/precalciner kilns.
- 191. Solid wastes used as alternative raw materials are typically fed into the kiln system via the normal raw meal supply, the same as traditional raw materials. However materials containing components that can be volatilised at low temperatures (for example, solvents) should be fed into the high temperature zones of the kiln system. Wastes containing volatile organic and inorganic components should not be fed via the normal raw meal supply unless controlled test runs in the kiln, or adequate laboratory tests, have demonstrated that undesired stack emissions can be avoided.
- 192. Combustible toxic compounds found in some hazardous waste, such as halogenated organic substances, need to be destroyed through proper temperature and residence time. In preheater/precalciner kilns, hazardous waste should generally be fed through either the main or the secondary burners. Hazardous and other wastes fed through the main burner, where conditions will

always be favourable, decompose under oxidising conditions at a flame temperature of >1800°C (see figure IV). Waste fed to a secondary burner, preheater or precalciner will be exposed to lower temperatures, though expected burning zone temperatures in the precalciner are typically >1000°C (UNEP, 2007). The kiln should be operated in such a way that the gas resulting from the process is raised, after the last injection of combustion air, in a controlled and homogeneous fashion and even under the most unfavourable conditions, to a temperature of 850 °C for two seconds (cf. Directive 2000/76/EC). In the case of hazardous wastes with a content of more than 1 per cent halogenated organic substances (expressed as chlorine), the temperature should be raised to 1100°C for at least two seconds. Under the United States TSCA disposal of PCBs requires a temperature of 1200°C and 2 seconds retention time (at 3 per cent excess oxygen in the stack gas).

Figure IV

Temperatures and residence times during cement manufacture

Characteristics	Temperature and time	δ
Temperature at main burner ① of the rotary kiln ②	>1450°C (material) >1800°C (flame temperature)	
Residence time at main burner	>12-15 seconds > 1200°C >5-6 seconds > 1800°C	
Temperature at precalciner ③	> 850°C (material) >1000°C (flame temperature)	3
Residence time at precalciner	> 2-6 seconds > 800°C	2 6668

- 193. For hazardous waste feeding into the kiln, the following should be conducted (EIPPCB, 2010):
- (a) To use the appropriate feed points to the kiln in terms of temperature and residence time depending on kiln design and kiln operation;
- (b) To feed waste materials containing organic components that can be volatilised before the calcining zone into the adequately high temperature zones of the kiln system;
- (c) To operate in such a way that the gas resulting from the process is raised, in a controlled and homogeneous fashion and even under the most unfavourable conditions, to a temperature of 850 °C for 2 seconds;
- (d) To raise the temperature to 1100 °C, if hazardous waste with a content of more than 1 per cent of halogenated organic substances, expressed as chlorine, is fed into the kiln;
  - (e) To feed wastes continuously and constantly;
- (f) To stop feeding waste when appropriate temperatures and residence times are not maintained or cannot be reached (at start-ups or shutdowns for instance), and whenever any emission limit value is exceeded.

## 2. Kiln operation control

- 194. The general principles of good operational control of the kiln system using conventional fuels and raw materials should also be applied to the use of waste. In particular, all relevant process parameters should be measured, recorded, and evaluated continuously. Kiln operators should undergo appropriate training for the requirements related to the use of hazardous waste, including health, safety, and environmental emission aspects.
- 195. For operational disruptions of the kiln, written work instructions describing the strategy to disconnect the hazardous waste feed to ensure minimum operational stability conditions should be available and known to the kiln operators.
- 196. The mineral content of the waste may affect the characteristics of the clinker. The raw mix composition should be adjusted accordingly to adhere to the given chemical set points. Input limits for chlorine, sulphur, and alkalis should be defined, and operational set points should be strictly observed. Bypass installations to avoid enrichment cycles of these compounds should only be considered if appropriate solutions for the management of the bypass dust generated have been identified.

- 197. It is important for combustion and process stability, for the purpose of controlling emissions of unintentionally formed POPs, to ensure (UNEP, 2007):
  - (a) Consistency in fuel characteristics (both alternative and fossil);
- (b) Consistency in fuel supply rate or frequency of introduction of batch-charged materials;
  - (c) That adequate excess oxygen is supplied to achieve good combustion;
- (d) That concentrations of CO in exhaust gases are monitored and do not exceed preestablished levels reflecting poor combustion conditions.

## C. Environmental aspects

#### 1. Air emissions

- 198. Whether or not wastes are being used in a cement plant, dust (particulate matter), NOx and SO2 emissions cause the greatest concern and needs to be dealt with. Other emissions to be considered are VOC, PCDDs, PCDFs, HCl, CO, CO2, HF, ammonia (NH3), benzene, toluene, ethylbenzene, xylene, polycyclic aromatic hydrocarbons (PAH), heavy metals and their compounds (EIPPCB, 2010). Under some circumstances, emissions may also include chlorobenzenes and PCBs (SBC, 2007). Sources of these emissions and BAT to prevent or reduce them (as defined within the European Union) are outlined in annex II.
- 199. Cement kilns co-processing hazardous wastes should comply with an emission limit for PCDDs/PCDFs of 0.1 ng I-TEQ/Nm3; 10. For other pollutants, pertinent national legislation should apply, for example:
  - (a) Chile: Supreme Decree N°45, 5 March 2007;11
- (b) European Union: Directive 2000/76/EC of the European Parliament and of the Council, of 4 December 200012; to be replaced in January 2014 by Directive 2010/75/EU;13
- (c) South Africa: National policy on thermal treatment of general and hazardous waste, Government Gazette (Staatskoerant), 24 July 2009;14
- (d) United States: Code of Federal Regulations, Title 40, Part 63 Subpart EEE, "National Emission Standards for Hazardous Air Pollutants from Hazardous Waste Combustors"15, and Part 60 Subpart F, "National Emission Standards for Hazardous Air Pollutants From the Portland Cement Manufacturing Industry and Standards of Performance for Portland Cement Plants".16
- 200. Competent authorities should consider establishing a maximum permissible period of any technically unavoidable stoppages, disturbances or failures of the purification devices or the measurement devices, during which the emissions into the air may exceed the prescribed emission limit values.
- 201. Control technologies are described by Greer (2003) and Karstensen (2008b). BAT and associated emission levels in the European Union are provided by the EIPPCB (2010). The European Commission's reference document includes information regarding available measures and techniques, such as description, applicability, cross-media effects, economics, etc. It provides useful information and best performance data on techniques to be considered as BAT.
- 202. Further guidance on BAT and provisional guidance on BEP for the prevention or minimization of the formation and subsequent release of unintentional POPs from cement kilns co-processing hazardous waste has been published by the Stockholm Convention Secretariat (UNEP, 2007). The

lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2010:334:0017:0119:EN:PDF

TEQ as referred to in Annex C, Part IV, paragraph 2 of the Stockholm Convention. Concentration expressed at normalized conditions of 11 per cent O2, 101.3 kPa, 273.15K, dry gas.

Available in Spanish from http://www.leychile.cl/Navegar?idNorma=265301

<sup>12</sup> Available from http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32000L0076:EN:NOT

<sup>13</sup> Available from http://eur-

<sup>14</sup> Available from http://us-cdn.creamermedia.co.za/assets/articles/attachments/22665 not 777.pdf

Available from http://ecfr.gpoaccess.gov/cgi/t/text/text-

idx?c=ecfr&rgn=div6&view=text&node=40:11.0.1.1.1.1&idno=40

NOx and SO2 limits for all cement kilns that were constructed, modified, or reconstructed after June 16, 2008. Available from http://www.gpo.gov/fdsvs/pkg/FR-2010-09-09/pdf/2010-21102.pdf

guidelines describe primary measures considered to be sufficient to achieve an emission level of PCDDs/PCDFs below 0.1 ng I-TEQ/Nm³ in flue gases for new and existing installations, and where these options do not lead to performance down to 0.1 ng I-TEQ/Nm³, secondary measures are cited, which are usually installed for the purpose of controlling pollutants other than unintentionally formed POPs, but that may also lead to a simultaneous reduction in emissions of chemicals listed in Annex C of the Stockholm Convention. (UNEP, 2007)

## 2. Cement kiln and bypass dust

- 203. All cement plants generate a fine dust from the kiln line, collectively labelled cement kiln dust (CKD). CKD composition varies, even over time from a single kiln line, but includes particulates representing the raw mix at various stages of burning, particles of clinker, and even particles eroded from the refractory brick and/or monolithic linings of the kiln tube and associated apparatus (Van Oss, 2005). Dust is also discarded from alkali bypass systems, installed to avoid excessive build-up of alkali, chloride and/or sulphur, however bypass dust, as opposed to CKD, consists of fully calcined kiln feed material.
- 204. In the European Union, BAT for process waste, in the cement manufacturing sector in general, is to re-use collected particulate matter in the process, wherever practicable, or to utilise these dusts in other commercial products, when possible. (EIPPCB, 2010).
- 205. To avoid disposal, most CKD and bypass dust is recycled directly back to the cement kiln or cement clinker grinder. In clinker manufacture, CKD partially offsets the need for raw materials such as limestone and natural rock constituents, thus avoiding the energy usage and emissions related to their extraction and processing. Periodically some dust may need to be removed from the system due to increasing concentrations of alkali, chloride and sulphur compounds that may compromise the quality of the clinker. Dust that cannot be recycled back into the process is removed from the system and often collected onsite in piles or monofills.
- 206. Where appropriate CKD not returned to the production process may be recovered in various types of commercial applications, including agricultural soil enhancement, base stabilizing for pavements, wastewater treatment, waste remediation, low-strength backfill and municipal landfill cover (United States EPA, 2011). These applications depend primarily on the chemical and physical characteristics of the CKD.
- 207. The major factors determining CKD characteristics are the raw feed material, type of kiln operation, dust collection systems, and fuel type. Since the properties of CKD can be significantly affected by the design, operation, and materials used in a cement kiln, the chemical and physical characteristics of CKD must be evaluated on an individual plant basis. (United States EPA, 2011) Until the degree of variability in the CKD has been established, frequent testing is recommended.
- 208. Depending upon the level of contaminants of concern (for example, heavy metals, POPs), this waste can in some cases be hazardous waste for which special handling and disposal measures apply (UNEP, 2007). A study by Karstensen (2006b) reports an average concentration of 6.7 ng I-TEQ/kg for PCDDs/PCDFs in CKD and a maximum concentration of 96 ng I-TEQ/kg. The same study shows that wastes from the cement industry have PCDD/PCDF levels in the same magnitude as foods such as fish, butter, breast milk, and less than the maximum permissible concentration of 100 ng TEQ/kg for sewage sludge applied to agricultural land.
- 209. To ensure the protection of public health and the environment and to prevent groundwater contamination, bypass dust or CKD, discarded from facilities that use hazardous wastes as supplementary fuels or raw materials, should be analyzed for metal and organic leachate quality parameters if they are to be disposed of on land. The analysis should be conducted during controlled test runs in addition to ongoing testing that may be required by local regulatory authorities. Releases of dust to the air should also be controlled.

#### 3. Emissions to water

210. In general, wastewater discharges are usually limited to surface run-off and cooling water only and cause no substantial contribution to water pollution (EIPPCB, 2010). Nevertheless, in the European Union the use of wet scrubbers is a BAT to reduce the emissions of SOx from the flue-gases of kiln firing and/or preheating/precalcining processes (EIPPCB, 2010). In this context, for cement kilns co-processing hazardous and other wastes in the European Union, the requirements of Directive 2000/76/EC for the discharge of wastewater from the cleaning for exhaust gases apply, so as to limit the transfer of pollutants from the air into water.

#### 4. End-product control

- 211. Final products such as clinker and cement are subject to regular control procedures required by the usual quality specifications as laid down in applicable national or international quality standards.
- 212. As a principle, co-processing should not alter the quality of the cement being produced. This means that the clinker, cement or concrete produced should not be used as a sink for heavy metals. There should be no negative impact on the environment as might be demonstrated with leaching tests on concrete or mortar, for example. The quality of cement should also allow end-of-life recovery.
- 213. Organic pollutants in the materials fed to the high temperature zone of the kiln system are nearly completely destroyed, while the inorganic components partition between the clinker product and CKD. Accordingly, the use of wastes in the clinker burning process may change the metal concentrations in cement products, and depending on the total input via the raw materials and fuels, the concentration of individual elements in the product may increase or decrease as a result of waste co-processing (EIPPCB, 2010). However, lengthy investigations have shown that the effect of waste on the heavy metals content of clinker is marginal on a statistical basis, the one exception being the bulk use of tires which will raise zinc levels (GTZ/Holcim, 2006).
- 214. As cement is blended with aggregates to form concrete or mortar, it is the behaviour of the metals within these building materials that is important for the evaluation of relevant environmental impacts of waste used in the production process. Studies have shown that metal emissions from concrete and mortar are low, and comprehensive tests have confirmed that metals are firmly incorporated in the cement brick matrix. In addition, dry-packed concrete offers high diffusion resistance, which further counteracts the release of metals. Tests on concrete and mortar have shown that the metal concentrations in the eluates are noticeably below those prescribed, for instance, by national legislation. Moreover, storage under different and partly extreme conditions has not led to any environmentally relevant releases, which also holds true when the sample material is crushed or comminuted prior to the leaching tests. (EIPPCB, 2010).
- 215. In regard to the above, the main results of leaching studies done to assess the environmental impacts of heavy metals embedded in concrete are as follows (GTZ/Holcim, 2006):
- (a) The leached amounts of all trace elements from monolithic concrete (service life and recycling) are below or close to the detection limits of the most sensitive analytical methods;
- (b) No significant differences in leaching behaviour of trace elements have been observed between different types of cements produced with or without alternative fuels and raw materials;
  - (c) The leaching behaviour of concrete made with different cement types is similar;
- (d) Leached concentrations of some elements such as chromium, aluminium and barium may, under certain test conditions, come close to limits given in drinking water standards; hexavalent chromium in cement is water-soluble and may be leached from concrete at a level higher than other metals, so chromium inputs to cement and concrete should be as limited as possible;
- (e) Laboratory tests and field studies have demonstrated that applicable limit values, for example, groundwater or drinking water specifications, are not exceeded as long as the concrete structure remains intact. For example, in primary or service life applications;
- (f) Certain metals such as arsenic, chromium, vanadium, antimony, or molybdenum may have a more mobile leaching behaviour, especially when the mortar or concrete structure is crushed or comminuted (for example, in recycling stages such as use as aggregates in road foundations, or in landfilling);
- (g) As there are no simple and consistent relations between the leached amounts of trace elements and their total concentrations in concrete or in cement, the trace element content of cements cannot be used as environmental criteria.
- 216. Assessments of the environmental quality of cement and concrete are typically based on the leaching characteristics of heavy metals to water and soil. Various exposure scenarios need to be considered (GTZ/Holcim, 2006):
- (a) Exposure of concrete structures in direct contact with groundwater ('primary' applications);
- (b) Exposure of mortar or concrete to drinking water in distribution (concrete pipes) or storage systems (concrete tanks) ('service life' applications);

- (c) Reuse of demolished and recycled concrete debris in new aggregates, road constructions, dam fillings etc. ('secondary' or 'recycling' applications);
  - (d) Dumping of demolished concrete debris in landfills ('end-of-life' applications).
- 217. Careful selection and monitoring of the waste ensure that the use of wastes does not result in metal emissions of any environmentally harmful magnitude (EIPPCB, 2010). However, in cases where the concentration of heavy metals exceeds the normal range found in cements made without waste, leaching tests on mortar and/or concrete should be conducted (GTZ/Holcim, 2006).
- 218. For "real-life" concrete and mortar exposure scenarios, different leaching tests and assessment procedures should be applied. Although standardized test procedures exist for waste management regulations and drinking water standards, there remains a need for harmonized and standardized compliance test procedures based on the exposure scenarios outlined above. It is recommended that a certified independent testing laboratory perform these at least annually.

# D. Monitoring

- 219. Emission monitoring should be conducted to allow authorities to check compliance with the conditions in operating permits and regulations, and to help operators manage and control the process, thus preventing emissions from being released into the atmosphere. It is the responsibility of the competent authority to establish and set appropriate quality requirements, and to consider a range of safeguards. For the purpose of compliance assessment use of the following is considered good practice (EIPPCB, 2003):
  - (a) Standard methods of measurement;
  - (b) Certified instruments:
  - (c) Certification of personnel;
  - (d) Accredited laboratories.
- 220. For self-monitoring activities the use of recognised quality management systems and periodic check by an external accredited laboratory instead of formal own accreditation can be appropriate (EIPPCB, 2003).
- 221. More useful information regarding monitoring principles can be found in the European Commission's Reference Document on the General Principles of Monitoring (EIPPCB, 2003).

#### 1. Process monitoring

- 222. To control kiln processes, continuous measurements are recommended for the following parameters (UNEP, 2007; EIPPCB, 2010):
  - (a) Pressure;
  - (b) Temperature;
  - (c) O2;
  - (d) NOx:
  - (e) CO;
- (f) SO2, when the SOx concentration is high (it is a developing technique to optimise CO with NOx and SO2).
- 223. In the European Union, the BAT conclusion for the cement manufacturing sector as a whole is to carry out monitoring and measurements of process parameters and emissions on a regular basis, such as (EIPPCB, 2010):
- (a) Continuous measurements of process parameters demonstrating process stability, such as temperature, O2, pressure, exhaust gas flow rate, and of NH3 emissions when using selective non-catalytic reduction (SNCR);
- (b) Monitoring and stabilising critical process parameters, for example, homogenous raw material mix and fuel feed, regular dosage and excess O2.

#### 2. Emissions monitoring

224. To accurately quantify the emissions, continuous measurements is BAT for the following parameters (UNEP, 2007):

- (a) Exhaust gas flow rate;
- (b) Moisture (humidity);
- (c) Temperature;
- (d) Dust (particulate matter);
- (e) O2;
- (f) NOx:
- (g) SO2;
- (h) CO.
- 225. Continuous measurement of TOC is also recommended. The operator should assure proper calibration, maintenance, and operation of the continuous emission monitoring systems (CEMS). A quality assurance programme should be established to evaluate and monitor CEMS performance on a continual basis.
- 226. Periodical monitoring at a minimum once per year is appropriate for the following substances:
  - (a) Metals (Hg, Cd, Tl, As, Sb, Pb, Cr, Co, Cu, Mn, Ni, V) and their compounds;
  - (b) HCl;
  - (c) HF;
  - (d) NH3;
  - (e) PCDDs/PCDFs.
- 227. The BAT according to EIPPCB (2010) is to carry out monitoring and measurements of process parameters and emissions on a regular basis, such as:
  - (a) Continuous measurements of dust, NOx, SOx and CO emissions;
  - (b) Periodic measurements of PCDDs/PCDFs and metals emissions;
  - (c) Continuous or periodic measurements of HCl, HF and TOC emissions.
- 228. In addition, for cement kilns co-processing hazardous and other wastes in the European Union, the requirements of Directive 2000/76/EC (to be replaced by Directive 2010/75/EU with effect from 7 January 2014) apply.
- 229. It is also possible to measure and monitor NH3 and Hg continuously, and to sample PCCDs/PCDFs and PCBs continuously for analysis from 1 to 30 days (EIPPCB, 2010).
- 230. Performance tests should be conducted to demonstrate compliance with the emission limits and performance specifications for continuous monitoring systems, when the kiln is operating under normal conditions.
- 231. Measurements of the following may be required under special operating conditions (UNEP, 2007; EIPPCB, 2010):
  - (a) Benzene, toluene and xylene (BTX);
  - (b) Polycyclic aromatic hydrocarbons (PAHs);
- (c) Other organic pollutants (for example, chlorobenzenes, PCBs including coplanar congeners, chloronaphthalenes, etc).
- 232. In case of hazardous waste disposal in cement kilns for the purpose of destruction and irreversible transformation of the POPs content in waste, the DRE should be determined (UNEP, 2007) and the reader is referred to the Updated General Technical Guidelines for the Environmentally Sound Management of Wastes Consisting of, Containing or Contaminated with Persistent Organic Pollutants (POPs) (SBC, 2007).

## 3. Environmental monitoring

233. Justifiable concerns about the environmental impact from the plant may require the implementation of an ambient air-monitoring programme. This should assess levels of key pollutants identified as a priority for environmental control. The arrangements should include control and downwind locations, including the area of maximum ground level deposition from stack emissions.

A meteorological station should be provided for the duration of the ambient sampling exercise in a location free from significant interference from buildings or other structures.

#### 4. Reporting requirements

- 234. Reporting of monitoring results involves summarising and presenting results, related information and compliance findings in an effective way. Good practice is based on consideration of: the requirements and audiences for reports, responsibilities for producing reports, the categories of reports, scope of reports, good reporting practices, legal aspects of reporting and quality considerations (EIPPCB, 2003)
- 235. Monitoring reports can be classified as follows (EIPPCB, 2003):
- (a) Local or basic reports, which are usually prepared by operators (for example, as part of their self-monitoring) and, where appropriate, should meet any permit requirements. These reports may concern, for example, an individual installation, an occurrence, which covers a short period and needs to be reported promptly, or local audiences;
- (b) National or strategic reports, which will generally be prepared by the competent authorities. These are usually summary reports and they typically concern, for example, several installations, longer periods in order to show trends, or national audiences;
- (c) Specialised reports, which are reports on relatively complex or novel techniques that are occasionally used to supplement more routine monitoring methods (for example, telemetry, neural networks, or deposition surveys).
- 236. Good practices in the reporting of monitoring information include (EIPPCB, 2003):
- (a) Data collection, which involves the acquisition of basic measurements and facts. Considerations of the following items are good practice in data collection: schedules (stating how, when, by whom and to whom the data are to be reported, and what types of data are acceptable); use of standard forms for collecting data; data qualification details (used to record whether data values are based on measurements, calculations or estimations); uncertainties and limitations data (details of detection limits, numbers of samples available); operational context details (details of the prevailing process operations and/or environmental conditions).
- (b) Data management, involving the organisation of data and its conversion into information. Considerations of the following items are good practice in data management: transfers and databases; data processing; software and statistics; and archiving.
- (c) Presentation of results, which involves the delivery of information to users in a clear and usable form. Considerations of the following items are good practice in the presentation of monitoring results, depending on the type of report: scope of the report (type of situation, timing requirements, location); programme of presentations; trends and comparisons; statistical significance (details on exceedences or changes that are significant when compared with the uncertainties in measurements and process parameters); interim performance (interim reports); strategic results (details on levels of compliance for different policies, activities, technologies, etc.); non-technical summaries (for the public); and distribution of reports.
- 237. In order for monitoring reports to be used in decision making processes they should be readily available and accurate (to within stated uncertainties). Good practice in accessibility and quality of the reports can be achieved by considering the following items: quality objectives and checks; competence; contingency arrangements; sign-off systems; retention of data; and falsification of data. (EIPPCB, 2003)
- 238. More useful information on monitoring principles can be found in the European Commission's Reference Document on the General Principles of Monitoring (EIPPCB, 2003).

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# Annex I

# Compilation of performance verification and trial burns results in cement kilns (Dr. Kare Helge Karstensen, personal communication, November 6, 2009)

# Introduction

- 1. Testing of cement kiln emissions for the presence of organic chemicals during the burning of hazardous materials has been undertaken since the 1970s, when the practice of combusting wastes in cement kilns was first considered. Lauber (1987), Ahling (1979) and Benestad (1989) describe some of these early tests on U.S., Swedish and Norwegian kilns, which confirmed the ability of cement kilns to destroy the organic component of a waste feed. For example, the DRE for chemicals such as methylene chloride, carbon tetrachloride, trichlorobenzene, trichloroethane and PCBs has typically been measured at 99.995 per cent and better.
- 2. Comprehensive emission studies have been performed when a conventional fuel such as coal was burned, and when hazardous waste was introduced, and these have generally concluded that no significant differences could be measured between usages of the two fuels. For example, Branscome et al (1985) observed that "no statistically significant increase in emission rates were observed when the waste fuel (as opposed to coal) was burned". Early studies on dioxin emissions have also come to this conclusion (Branscome et al. (1985), Lauber (1987) and Garg (1990)).

## A. Results from trial burns conducted in the 1970s

- 3. In the mid-1970s, a series of tests were conducted at the St. Lawrence cement plant in Canada to measure the destruction of various chlorinated waste streams being fed into their wet process cement kiln. The overall DRE established for the chlorinated compounds was greater than 99.986 per cent. This value was considered to be artificially low because the water used to slurry the raw feed was contaminated with low molecular weight chlorinated compounds.
- 4. In 1978, a series of tests was conducted at the Stora Vika Cement Plant in Sweden to evaluate the efficiency of their wet process cement kiln in destroying various chlorinated waste streams. Although chloroform was found in the stack gas, the majority of the chlorinated compounds were not detected. A DRE greater than 99.995 per cent was determined for methylene chloride and a DRE greater than 99.9998 per cent was demonstrated for trichloroethylene.

## B. Results from trial burns conducted in the 1980s

5. Trial burns conducted in the 1980s continued to demonstrate that high DREs could be obtained for the organic constituents in the hazardous waste fuel burned in cement kilns. The results of trial burns of one wet and one dry process cement kiln illustrate the typical values obtained for DREs. The principle organic hazardous constituents selected for the trial burns were methylene chloride, 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), methyl ethyl ketone, 1,1,1-trichloroethane and toluene. As summarized in the table below, the majority of the DREs were greater than 99.99 per cent. DREs less than 99.99 per cent resulted from either laboratory contamination problems or improper selection of the POHCs.

Table 1. Average DREs for a wet and a dry process cement kiln

Selected POHCs	Wet process kiln	Dry process kiln
Methylene chloride	99.983 %	99.96 %
Freon 113	>99.999 %	99.999 %
Methyl ethyl ketone	99.988 %	99.998 %
1,1,1-Trichloroethane	99.995 %	>99.999 %
Toluene	99.961 %	99.995 %

#### C. Results from trial burns conducted in the 1990s

6. Trial burns conducted in the 1990s have focused on the selection of compounds as POHCs that would not typically be present as contaminants or generated as PICs from the combustion of conventional fuel. Use of this criterion has resulted in more accurate DREs being obtained.

- 7. In a DRE testing of a dry process cement kiln equipped with a preheater, carbon tetrachloride and trichlorobenzene were chosen as the POHCs. When fed to the burning zone of the kiln, DREs obtained were greater than 99.999 per cent for carbon tetrachloride and greater than 99.995 per cent for trichlorobenzene. To determine the limits of the system, DREs were also determined when these POHCs were fed to the kiln inlet (i.e. cool end) of the kiln along with tyres. DREs obtained were greater than 99.999 per cent for carbon tetrachloride and greater than 99.996 % for trichlorobenzene.
- 8. DRE testing conducted at a cement kiln owned by United Cement supports the foregoing results. Sulphur hexafluoride was chosen as the POHC because of its thermal stability and ease of measurement in the stack gases. In addition, "contamination" problems and PIC interferences are unlikely with the use of this compound. DREs greater than 99.9998 per cent were obtained in every case.
- 9. In 1999 a test burn with pesticide contaminated soil fed into the kiln inlet was performed in a dry process kiln in Colombia. The test burn result showed a DRE of >99.9999 per cent for all the introduced pesticides.

## D. Results from recent trial burns

- 10. A test burn with two expired chlorinated insecticide compounds introduced at a rate of 2 tons per hour through the main burner was carried out in Vietnam in 2003. The DRE for the introduced insecticides was >99.99999 per cent.
- 11. A three day test burn in Sri Lanka in 2006 demonstrated that the cement kiln was able to destroy PCB in an irreversible and environmental sound manner without causing any new formation of PCDD/PCDF or HCB. The destruction and removal efficiency (DRE) was better than 99.9999 per cent at the highest PCB feeding rate.
- 12. A five day test burn with POPs contaminated soil was conducted in a cement kiln in Venezuela in 2007. The soil was contaminated with relatively low levels of various chlorinated pesticides, first of all the aldrin, dieldrin and endrin (up to max 551 mg/kg). Measurement showed the same low levels of dieldrin in the stack gas ( $<0.019 \,\mu\text{g/Nm}^3$ ) when no contaminated soil was fed as when feeding 2 tonne/h of contaminated soil containing up to 522 mg dieldrin/kg. It can therefore be assumed that the measured DRE of 99.9994 per cent achieved with the highest feeding concentration is probably higher in reality.
- 13. A recent study evaluating more than 2000 PCDD/PCDF cement kiln measurements and indicating that most modern cement kilns co-processing waste (also organic hazardous wastes) can meet an emission level of 0.1 ng PCDD/PCDF I-TEQ/m³.

## E. Summary

- 14. Earlier data, which indicated cement kiln DRE results below 99.99 per cent are most probably either from outdated sources or improperly designed tests, or both. In the early years of development of this concept and the sampling and analytical techniques to evaluate its environmental performance, there were several instances where POHCs were selected that did not meet the necessary criteria. For example, a major problem with many early tests was that the POHCs selected for DRE evaluation were organic species that are typically found at trace levels in the stack emissions from cement kilns that burn solely fossil fuel. While these PICs were emitted at very low levels, they nonetheless greatly interfered with the measurement of POHC destruction. Practitioners quickly learned that DRE could not be properly measured if POHCs used in testing were chemically the same or closely related to the type of PICs routinely emitted from raw materials. For that reason, early DRE test results (i.e., before 1990) should always be treated with caution.
- 15. In some cases however, operational factors during the testing or sampling and analytical techniques contributed to the low DRE results. These typically were problems that occurred only in the earliest tests conducted during the developmental stages of this technology and should be possible to avoid today. Trial burn is a good way of demonstrating a kilns performance and ability to destroy wastes in an irreversible and sound way, but the design and the conditions of the trial is very crucial.

## F. Early applications of trial burn rules to cement kiln evaluation

16. Since the early nineteen seventies, the United States EPA, several state agencies, Canadian, Norwegian, Swedish agencies have conducted studies of the feasibility of using cement kilns for hazardous waste destruction. These wastes have included a broad range of chlorinated hydrocarbons, aromatic compounds, and waste oils. Both wet and dry process cement kilns, aggregate kilns and lime kilns have been used for these tests.

17. The available reports on cement kilns provides data about performance with regard to the following specific compounds: trichloromethane (chloroform); dichloromethane (methylene chloride); carbon tetrachloride; 1,2-dichloroethane; 1,1,1-trichloroethane; trichloroethylene; tetrachloroethylene; 1,1,2-trichloro-1,2,2-trifluorethane (Freon 113); chlorobenzene; benzene; xylene; toluene; 1,3,5-trimethylbenzene; methyl ethyl ketone; methyl isobutyl ketone; carbon hexafluorine; phenoxy acids; chlorinated hydrocarbons; chlorinated aliphatics; chlorinated aromatics; PCBs; and POPs pesticides.

Table 2. Summary of DREs for selected compounds from the seventies and the eighties

Site	POHC or waste component	DRE
St. Lawrence Cement (Canada)	Chlorinated aliphatics	>99.990
	Chlorinated aromatics	>99.989
	PCBs	>99.986
Stora Vika (Sweden)	Methylene chloride	>99.995
	Trichloroethylene	>99.9998
	All chlorinated hydrocarbons	>99.988
	PCBs	>99.99998
	Chlorinated phenols	>99.99999
	Phenoxy acids	>99.99998
	Freon 113	>99.99986
Brevik (Norway)	PCBs	>99.99999
San Juan Cement (Puerto Rico)	Methylene chloride	93.292-99.997
	Trichloromethane	92.171-99.96
	Carbon tetrachloride	91.043-99.996
Portland (Los Robles)	Methylene chloride	>99.99
	1,1,1-Trichloroethane	99.99
	1,3,5-Trimethylbenzene	>99.95
	Xylene	>99.99
General Portland (Paulding)	Methylene chloride	99.956-99.998
	Freon 113	>99.999
	Methyl ethyl ketone	99.978-99.997
	1,1,1-trichloroethane	99.991-99.999
	Toluene	99.940-99.988
Lone Star Industries (Oglesby)	Methylene chloride	99.90-99.99
	Freon 113	99.999
Y 7	Methyl ethyl ketone	99.997-99.999
	1,1,1-trichloroethane	>99.999
	Toluene	99.986-99.998
Marquette Cement (Oglesby)	Methylene chloride	99.85-99.92
	Methyl ethyl ketone	99.96
	1,1,1-trichloroethane	99.60-99.72
	Toluene	99.95-99.97
Rockwell Lime	Methylene chloride	99.9947-99.9995
	Methyl ethyl ketone	99.9992-99.9997
	1,1,1-trichloroethane	99.9955-99.9982
	Trichloroethylene	99.997-99.9999
	-	

Site	POHC or waste component	DRE
	Tetrachloroethylene	99.997-99.9999
	Toluene	99.995-99.998
Site I	1,1,1-trichloroethane	99.88-99.98
	Trichloroethylene	99.8-99.994
	Benzene	82.5-98.5
	Tetrachloroethylene	99.87-99.989
	Toluene	99.7-99.90
	Chlorobenzene	99.3-99.4
	Methyl ethyl ketone	99.93-99.98
	Freon 113	99.988-99.998
Site II	Methylene chloride	>99.99996->99.99998
	1,2-dichloroethane	99.91->99.993
	1,1,1-trichloroethane	99.9998-99.9999
	Carbon tetrachloride	99.8-99.995
	Trichloroethylene	99.996-99.9993
	Benzene	99.75-99.93
	Tetrachloroethylene	99.998-99.9998
	Toluene	99.997-99.9998
	Chlorobenzene	99.92-99.97
	Methyl ethyl ketone	99.996->99.999992
	Freon 113	99.99991-99.99998
Florida Solite Corp.	Methyl ethyl ketone	99.992-99.999
	Methyl isobutyl ketone	99.995-99.999
	Tetrachloroethylene	99.995-99.999
	Toluene	99.998-99.999

Source: EPA (1986)

- 18. It should be noted that the DRE calculations did not include corrections for test compounds measured during baseline tests.
- 19. The issue of PIC formation is one about which there is generally great public concern. Some of the kiln tests demonstrated minor increases in PICs resulting from waste combustion. However, tests run on coal-fired facilities demonstrate that PICs are virtually inevitable for these systems. Although trace quantities (<23 parts per trillion) of polychlorinated dibenzodioxins and dibenzofurans were measured at San Juan during a kiln upset, and trace quantities may have been present at Stora Vika, the EPA summary report concludes that they are not confirmed as PICs from waste production.
- 20. If waste liquid organic chemicals are fed into the firing end of the cement kiln, it can be readily seen that they will be subject to the high temperatures and long residence times of the cement clinker production process. Consequently, they will be almost completely destroyed by a combination of pyrolysis and oxidation.

## Annex II

## **Sources of air emissions**

#### A. Particulate matter

- 1. The cement production process includes thermal treatment (drying, heating, calcining, clinkerization, cooling) of materials through direct contact with hot gases. It also includes pneumatic material transports and material classification and separation. At the end of these processes, air, gas and pulverized materials have to be separated. Incomplete separation gives rise to dust emissions kiln/raw mill main stack, clinker cooler stack, cement mill stacks, material transfer point dedusting air outlets.
- 2. In the European Union, BAT for dust emissions arising from dusty operations other than those from kiln firing, cooling and main milling processes, is to reduce channelled dust emissions from dusty operations (taking into account a maintenance management system) to less than 10 mg/Nm³ (BAT associated emission level or BAT-AEL), as the average over the sampling period (spot measurement, for at least half an hour) by applying dry exhaust gas cleaning with a filter. BAT for dust emissions arising from kiln firing processes is to reduce dust (particulate matter) emissions from flue-gases of kiln firing processes by applying dry exhaust gas cleaning with a filter. The BAT-AEL is <10-20 mg/Nm³, as the daily average value. When applying fabric filters or new or upgraded ESPs, the lower level is achieved. (EIPPCB, 2010)

# B. Sulphur oxides

- 3.  $SO_2$  results from the oxidation of sulphide or elemental sulphur contained in the fuel during combustion. In addition, sulphide or elemental sulphur contained in raw materials may be 'roasted' or oxidized to  $SO_2$  in areas of the kiln system where sufficient oxygen is present and the material temperature is in the range of 300-600°C. Sulphates in the raw mix can also be converted to  $SO_2$  through localized reducing conditions in the kiln system. The alkaline nature of the cement provides for direct absorption of  $SO_2$  into the product, thereby mitigating the quantity of  $SO_2$  emissions in the exhaust stream.
- 4. Range of emissions depends on content of volatile sulphur compounds in raw materials: mostly below 300 mg/Nm³; sometimes up to 3000 mg/Nm³.
- 5. In the European Union, BAT for SOx emissions is to keep the emissions of SOx low or to reduce the emissions of SOx from the flue-gases of kiln firing and/or preheating/precalcining processes by applying one of the following measures/techniques: absorbent addition or wet scrubber. (EIPPCB, 2010)
- 6. BAT associated emission levels for SOx are (EIPPCB, 2010):

Parameter	Unit	BAT-AEL (daily average value) (a)
SOx expressed as SO <sub>2</sub>	mg/Nm <sup>3</sup>	<50 - <400

(a) The range takes into account the sulphur content in the raw materials

# C. Nitrogen oxides

- 7. Of the four mechanisms of NOx formation in cement kilns, thermal and fuel NOx formation are the most important. Thermal NOx results from the oxidation of molecular nitrogen in air at high temperature. This occurs in and around the flame in the burning zone of a cement kiln at a temperature greater than 1200°C.
- 8. Fuel NOx results from the oxidation of nitrogen in the fuel at any combustion temperature found in the cement process. Because of the lower combustion temperature in the calciner and some sites of supplemental fuel combustion, the formation of fuel NOx often exceeds that of thermal NOx at these locations.
- 9. The generation of feed NOx has been demonstrated only in the laboratory by heating nitrogen-containing cement raw materials to the range of 300-800°C in the presence of oxygen. Slow heating, such as occurs in wet and long-dry kilns, appears to increase the yield of NOx for a given raw material. The yield of feed NOx is potentially lower when the raw material is heated quickly in a preheater or precalciner system. Prompt NOx is generated by the reaction of certain fuel-derived radicals with elemental nitrogen in a hydrocarbon flame and is a minor contributor to overall NOx generation.
- 10. Range of emissions (unabated) is 300 to 2000 mg/Nm<sup>3</sup>.

- 11. In the European Union, BAT for NOx emissions is to reduce the emissions of NOx from the flue-gases of kiln firing processes by applying the following measures/techniques individually or in combination (EIPPCB, 2010):
- (a) Primary measures/techniques, such as: flame cooling; low NOx burners; mid kiln firing; addition of mineralisers to improve the burnability of the raw meal (mineralised clinker); process optimisation;
- (b) Staged combustion (conventional or waste fuels), also in combination with a precalciner and the use of optimised fuel mix;
  - (c) SNCR;
  - (d) SCR, subject to appropriate catalyst and process development in the cement industry.
- 12. BAT associated emission levels for NOx are (EIPPCB, 2010):

Kiln type	Unit	BAT-AEL (daily average value)
Preheater kilns	mg/Nm <sup>3</sup>	<200 – 450 (b)
Lepol and long rotary kilns	mg/Nm <sup>3</sup>	400 – 800 (a)

- (a) Depending on initial levels and ammonia slip.
- (b) BAT-AEL is 500 mg/Nm3, where after primary measures/techniques the initial NOx level is >1000 mg/Nm3. Existing kiln system design, fuel mix properties including waste, raw material burnability can influence the ability to be in the range. Levels below 350 mg/Nm3 are achieved at kilns with favourable conditions. The lower value of 200 mg/Nm3 has only been reported as monthly average for three plants (easy burning mix used).

## D. Carbon oxides

13. CO is a PIC of carbonaceous fuels resulting from insufficient oxygen at the combustion site, insufficient mixing of oxygen and fuel at the combustion site, plus rapid cooling of the combustion products to below the ignition temperature of CO prior to its complete oxidation. CO can be formed unintentionally at any of the combustion sites in the kiln system. The emission of CO usually represents partially burned and under utilized fuel.

However, as a result of using oxygen-deficient combustion in the riser duct or calciner as a NOx control strategy, CO can sometimes be generated in the pyroprocess and may appear in the flue gas discharge if it is not subsequently oxidized following its formation.

14.  $CO_2$  results from the combustion of carbonaceous fuel and the calcination of the calcareous component of the raw material mix, an unavoidable and fixed consequence of cement manufacture. Of the total amount of  $CO_2$  emitted from a cement kiln, about half originates from the raw material while the remainder originates from the combustion process. About one tonne of  $CO_2$  is emitted per tonne of clinker produced. More thermally efficient systems emit slightly less while less thermally efficient systems emit slightly more.

#### E. Organic emissions

- 15. VOC emissions from cement kilns are of interest because of their role in the formation of atmospheric ozone and the designation of some VOC as hazardous air pollutants. Total hydrocarbons (THCs) emissions (of which VOCs are a subset) are primarily generated as a result of evaporation and/or cracking of the constituents of petroleum and kerogens found in the raw material mix.
- 16. The potential for organic emissions varies with the selection of raw materials and the variability of the concentration of organic constituents within raw material sources. Organic PICs also can be formed as a result of incomplete combustion at any of the combustion sites within a pyroprocessing system.
- 17. Range of emissions is dependant on content of raw materials of volatile organics: mostly below 50 mg/Nm<sup>3</sup>; sometimes up to 500 mg/Nm<sup>3</sup>.
- 18. In the European Union, BAT for TOC emissions is to keep the emissions of TOC from the flue-gases of the kiln firing processes low by applying the following measure/technique: avoid feeding raw materials with a high content of volatile organic compounds into the kiln system via the raw material feeding route. Moreover, facilities co-processing hazardous and other wastes that are located in the European Union have to meet the requirements of the Council Directive 2000/76/EC.

## F. Acid gases

- 19. All the oxidants necessary to convert  $SO_2$  to sulphur trioxide ( $SO_3$ ) are present in the combustion products of fossil fuel. Therefore, emissions of  $SO_3$  and/or  $H_2SO_4$  mist are a possibility from cement plants. The emissions of  $H_2SO_4$  mist may also increase in those plants employing 'tailpipe wet scrubbers'.
- 20. If fluorine is naturally present in the raw materials or added as a mineralizer, the emission of HF from a cement kiln system becomes a possibility.
- 21. How HCl formed in cement kilns is not fully understood. Nevertheless, there is limited evidence that HCl emissions may be independent of chlorine input to a kiln system, possibly due to the affinity of chlorine for calcium and alkali metals. Emissions can result if inputs exceed the capacity of the clinker to absorb inbound chlorine.
- 22. Range of HCl emissions: SP/PC17 kiln systems, <10 mg/Nm<sup>3</sup>; wet kilns, up to 80 mg/Nm<sup>3</sup>.
- 23. In the European Union, BAT is to keep the emissions of HCl below 10 mg/Nm³ (BAT-AEL), as the daily average value or average over the sampling period (spot measurements, for at least half an hour), by applying the following primary measures/techniques individually or in combination: using raw materials and fuels containing a low chlorine content, and/or limiting the amount of chlorine content for any waste that is to be used as raw material and/or fuel in a cement kiln. (EIPPCB, 2010)
- 24. Similarly, BAT is to keep the emissions of HF below 1 mg/Nm³ (BAT-AEL) expressed as HF, as the daily average value or average over the sampling period (spot measurements, for at least half an hour), by applying the following primary measure/technique individually or in combination: using raw materials and fuels containing low fluorine and/or limiting the amount of fluorine content for any waste that is to be used as raw material and/or fuel in a cement kiln. (EIPPCB, 2010)

#### G. Ammonia

- 25. Trace quantities of NH<sub>3</sub> in the exhaust gas from a cement kiln gas probably result from the pyrolysis of nitrogenous compounds in fossil fuels and raw materials. Ammonia emissions from cement kilns are of primary concern because of the potential contribution to regional haze. In addition, atmospheric reactions occur just outside of the stack between NH<sub>3</sub> and the oxides of sulphur or HCl that produce ammonium sulphate, ammonium bisulphate, or ammonium chloride as very fine particulate matter (PM) and These reaction products are observed as the undesirable anomaly known as a 'detached plume'. Depending on the location of the stack observer, the detached plume can give the incorrect appearance of poorly controlled PM emissions from a kiln stack.
- 26. Range of emissions is <1 to 15 mg/Nm<sup>3</sup> as a rule with exceptions up to 40 mg/Nm<sup>3</sup>.

# H. Benzene

- 27. Benzene might be present in conventional and alternative raw materials and is partially roasted off at material preheating.
- 28. Range of emissions, normally 1 to 2 mg/Nm<sup>3</sup>; up to 3 and more mg/Nm<sup>3</sup> in rare cases

## I. Heavy Metals

- 29. Heavy metals are ubiquitous in all cement kiln input materials. Since clean gas dust (i.e., dust after the dedusting equipment) is an input materials fraction, it also contains heavy metals. In addition, semi-volatile and volatile heavy metals are evaporated and condense (predominantly) on the fine dust fraction.
- 30. Most heavy metal emissions remain below the detection limits, and all emissions, except for mercury, remain safely below generally adopted limit values. Mercury emissions can exceed 0.05 mg/Nm<sup>3</sup> in case of excessive inputs with materials.
- 31. In the European Union, BAT for metal emissions is to minimise the emissions of metals from the flue-gases of the kiln firing processes by applying the following measures/techniques individually or in combination (EIPPCB, 2010):
- (a) Selecting materials with a low content of relevant metals and limiting the content of relevant metals in materials, especially mercury;

<sup>17</sup> SP = Suspension Preheater kiln; PC = Precalciner kiln

- (b) Using a quality assurance system to guarantee the characteristics of the waste materials used:
  - (c) Using effective dust removal measures/techniques.
- 32. BAT associated emission levels for metal emissions are (EIPPCB, 2010):

Metals	Unit	BAT-AEL (average over the sampling period (spot measurements, for at least half an hour))
Hg	mg/Nm <sup>3</sup>	<0.05 (b)
Cd + Tl	mg/Nm <sup>3</sup>	<0.05 (a)
Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V		<0.5 (a)

- (a) Low levels have been reported (EIPPCB, 2010).
- (b) Low levels have been reported (EIPPCB, 2010). Values higher than 0.03 mg/Nm3 have to be further investigated. Values close to 0.05 mg/Nm3 require consideration of additional measures/techniques such as those described in EIPPCB (2010).

# J. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans

- 33. Dioxins, furans or advanced precursors that might be present in conventional raw materials (rarely) or wastes used as alternative raw materials, are partially roasted off at material preheating. Any chlorine input in the presence of organic material may potentially cause the formation of PCDD and PCDF in heat (combustion) processes. PCDD/PCDF can be formed by the 'de novo synthesis mechanism' in or after the preheater and in the air pollution control device if chlorine and hydrocarbon precursors are available in sufficient quantities in the temperature range 200° C to 450° C.
- 34. A comprehensive survey of PCDD/PCDF emissions from cement kilns, in developed and developing countries, is given in a report by Karstensen (2006b).
- 35. In a survey performed by CEMBUREAU, PCDD and PCDF measurements from 110 cement kilns in 10 European countries were presented. The average concentration, taking into account all of the data in this dataset, was 0.016 ng I-TEQ/m<sup>3</sup>. The range between the lowest and highest concentrations measured was < 0.001 to 0.163 ng I-TEQ/m<sup>3</sup>. All measurements were expressed corrected to standard conditions (dry gas, 273 K, 101.3 kPa and 10 per cent  $O_2$ ).
- 36. A report from the Holcim Cement Company, which operates cement kilns worldwide, gives average PCDD/PCDF values for 2001 and 2002 as 0.041 ng TEQ/Nm³ (71 kilns) and 0.030 ng TEQ/Nm³ (82 kilns) respectively. Of these measurements, 120 were from countries within the Organisation for Economic Co-operation and Development (OECD), with an average value of 0.0307 ng TEQ/Nm³; the minimum and maximum values measured were 0.0001 and 0.292 ng TEQ/Nm³ respectively, with nine long wet kilns being above 0.1 ng TEQ/Nm³. For the 29 measurements from non-OECD countries, the average value was 0.0146 ng TEQ/Nm³; the minimum and maximum values measured were 0.0002 and 0.074 ng TEQ/Nm³ respectively, with no measurements being above 0.1 ng TEQ/Nm³.
- 37. The PCDD/PCDF data presented by Karstensen (2006b) shows that:
- (a) Most cement kilns can meet an emission level of 0.1 ng TEQ/Nm3 if primary measures are applied;
- (b) Co-processing of waste fed to the main burner, kiln inlet or the precalciner does not seem to influence or change the emissions of POPs;
- (c) Data from dry preheater and precalciner cement kilns in developing countries show emission levels much lower than 0.1 ng TEQ/Nm3.
- 38. In the European Union, BAT is to avoid emissions of PCDDs/PCDFs or to keep the emissions of PCDDs/PCDFs from the flue-gases of the kiln firing processes low by applying the following measures/techniques individually or in combination (EIPPCB, 2010):
- (a) Carefully selecting and controlling of kiln inputs (raw materials), i.e. chlorine, copper and volatile organic compounds;
  - (a) Carefully selecting and controlling of kiln inputs (fuels), i.e. chlorine and copper;
  - (b) Limiting/avoiding the use of wastes which contain chlorinated organic materials;

- (c) Avoid feeding fuels with a high content of halogens (e.g. chlorine) in secondary firing;
- (d) Quick cooling of kiln exhaust gases to lower than 200 °C and minimising residence time of flue-gases and oxygen content in zones where the temperatures range between 300 and 450 °C;
  - (e) Stop feeding waste for operations such as start-ups and/or shutdowns.
- 39. The BAT-AELs are <0.05-0.1 ng PCDD/F I-TEQ/Nm3, as the average over the sampling period (6-8 hours) (EIPPCB, 2010).

# K. Hexachlorobenzene and polychlorinated biphenyls

40. Hexachlorobenzene (HCB) and PCB have not been the subject of regulatory monitoring in cement plants to date. Most measurements that have taken place have not detected HCB emissions. As regards PCB emissions, 40 measurements carried out in 13 kilns in Germany in 2001 revealed a maximum concentration of  $0.4~\mu g$  PCB /Nm³; in nine of the 40 measurements, no PCB were detected. From Vietnam co-processing of pesticides has shown emissions of dioxin like PCB of 0.001~ng TEQ/m³ and HCB emissions below the detection limit of 31~ng/m³.

Sources: EIPPCB (2010), GTZ/Holcim (2006), UNEP (2007), Karstensen (2006b), Greer (2003)

