Pavojingų atliekų, kaip alternatyvaus kuro panaudojimas cemento gamyboje

Preamble

These technical guidelines provide general guidance on co-processing of waste as alternative fuels and raw materials in cement production in accordance with provisions of the Basel Convention.

The Basel Convention emphasizes, amongst other principles, environmentally sound management (ESM) of hazardous and other wastes, which is defined as taking all practicable steps to ensure that hazardous and other wastes are managed in a manner that will save natural resources, and will protect human health and the environment against the adverse effects which may result from such wastes. The Basel Convention requires that Parties take the appropriate measures to "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" and to "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". Countries should therefore strive for greater self-sufficiency in hazardous waste management where this is technically and economically feasible

Co-processing of waste materials in properly controlled cement kilns provides energy and materials recovery while cement is being produced and offers an environmentally sound recovery option for many of society's wastes. Particularly in developing nations, which may have little or no waste management infrastructure, properly designed and operated cement kilns can provide a practical, cost-effective and environmentally preferred option (in line with the Waste Management Hierarchy) to landfill and incineration, through the co-processing of waste materials. Co-processing of waste in the resource-intensive industries in general, can be an important element in a more sustainable system of managing raw materials and energy.

Although the substitution of fossil fuels with alternatives is viewed by some stakeholders and jurisdictions in the same light as incineration, it is nevertheless a well-developed practice in a number of countries, and some national governments actively promote this approach, provided that stringent requirements with regard to input, process and emission control are met.

These guidelines are considered to be current best practice at the time of writing and should not be regarded as providing a conclusive indication of appropriate action. Neither should they be regarded as prescriptive or a clear recommendation to use an option in all cases. They provide a general orientation concerning the conditions in which co-processing can be applied and will require regular update in order to incorporate advances as they arise.

These technical guidelines refer to both hazardous and nonhazardous waste, although the emphasis is on the former as defined by the Basel Convention. These guidelines do not cover quarrying or the re-use of concrete, nor the substitution of blast furnace slag (recycled from steel production) and fly ash (recovered from coal driven power stations) for clinker.

Revision date: 22/03/2010

Glossary

Accuracy: A measure of the overall agreement of a measurement to a known value; includes a combination of random error (precision) and systematic error (bias) components of both sampling and analytical operations.

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

Alkali bypass: A duct between the feed end of the kiln and the preheater tower through which a portion of the kiln exit gas stream is withdrawn and quickly cooled by air or water to avoid excessive build-up of alkali, chloride and/or sulphur on the raw feed. This may also be referred to as the '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, like coal. These are sometimes termed secondary, substitute or waste-derived fuels, among others.

Alternative raw materials: Wastes containing useful minerals such as calcium, silica, alumina, and iron used as raw materials in the kiln, replacing raw materials such as clay, shale, and limestone. These are sometimes termed secondary or substitute raw materials.

Audit: A systematic and independent examination to determine whether quality activities and related results comply with planned arrangements and whether these arrangements are implemented effectively and are suitable to achieve objectives.

Best available techniques (BAT): The most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.

Bypass dust: Discarded dust from the bypass system dedusting unit of suspension preheater, precalciner and grate preheater kilns, consisting of fully calcined kiln feed material.

Calcination: The heat-induced removal, or loss, of chemically-bound volatiles, usually other than water. In cement manufacture it involves the thermal decomposition of calcite (calcium carbonate) and other carbonate minerals to 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 material comprising CKD is actually unreacted raw material, including raw mix at various stages of burning and particles of clinker. The term CKD is sometimes used to denote all dust from cement kilns, i.e. also from bypass systems.

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

Clinkering: The thermochemical formation of the actual clinker minerals, especially to those reactions occurring above about 1300°C; also the zone in the kiln where this occurs. Also known as sintering or burning.

Comparability: A qualitative term that expresses the measure of confidence that one data set can be compared to another and can be combined for the decision(s) to be made.

Completeness: A measure of the amount of valid data needed to be obtained from a measurement system.

Concrete: Building material made by mixing a cementing material (such as portland cement) along with aggregate (such as sand and gravel) with sufficient water and additives to cause the cement to set and bind the entire mass.

Conventional (fossil) fuels: Non-renewable carbon-based fuels traditionally used by the cement industry, including coal and oil.

Co-processing: The use of 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:

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

where W_{in} is the mass feed rate of one principal organic hazardous constituent (POHC) in the waste stream fed to the kiln, and $W_{\mathrm{out\ stack}}$ 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:

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

where W_{in} is the mass feed rate of one principal organic hazardous constituent (POHC) in the waste stream fed to the kiln, and $W_{\mathrm{out\ combustion\ chamber}}$ 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 which is emitted.

Disposal: Any operation specified in Annex IV to the Basel Convention (“Disposal operations”)

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 (raw meal). The dry process is less energy consuming than the wet process, where water is added to the raw materials during grinding to form a slurry.

Emissions testing: Manual collection of stack gas sample(s), followed by chemical analysis to determine pollutant concentrations.

Environmental impact assessment (EIA): An examination, analysis and assessment of planned activities with a view to ensuring environmentally sound and sustainable development. Criteria for determining the requirement for an EIA should be clearly defined in legal/policy sources.

Environmentally sound management (ESM): 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.

Hazardous wastes: Wastes that belong to any category contained in Annex I to the Basel Convention ("Categories of wastes to be controlled"), unless they do not possess any of the characteristics contained in Annex III to the Convention ("List of hazardous characteristics"): explosive; flammable liquids; flammable solids; substances or wastes liable to spontaneous combustion; substances or wastes which, in contact with water, emit flammable gases; oxidizing; organic peroxides; poisonous (acute); infectious substances; corrosives; liberation of toxic gases in contact with air or water; toxic (delayed or chronic); ecotoxic; capable, by any means, after disposal, of yielding another material, e.g. leachate, which possesses any of the other characteristics.

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 these are 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. It is sometimes called the gross heat value.

Hydraulic cement: A cement that sets and hardens by chemical interaction with water and that is capable of doing so under water.

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

Kiln: The heating apparatus in a cement plant in which clinker is manufactured. Unless otherwise specified, may be assumed to refer to a rotary kiln.

Life Cycle Assessment (LCA): objective process to evaluate the environmental burdens associated with a product, process or activity by identifying and quantifying energy and materials used and wastes released to the environment, to assess the impact of those energy and materials uses and releases to the environment, and to evaluate and implement opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process or activity, encompassing extracting and processing raw materials; manufacturing, transportation and distribution; use, reuse and maintenance; recycling and final disposal.

Lower heating (calorific) value (LHV): The higher heating value less the latent heat of vaporisation of the water vapour formed by the combustion of the hydrogen in the fuel. It is sometimes called the net heat value.

Manifest: Shipping document that travels with hazardous waste from the point of generation, through transportation, to the final disposal facility, creating a 'cradle-to-grave' tracking of the hazardous waste.

Operator: Any natural or legal person who operates or controls the installation or facility.

Portland cement clinker: A hydraulic material which consists of at least two-thirds by mass of calcium silicates ($(CaO)_3 \cdot SiO_2$ and $(CaO)_2 \cdot SiO_2$), the remainder containing aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3) and other oxides.

Portland cement: A hydraulic cement produced by pulverising Portland-cement clinker, and usually containing calcium sulphate.

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 the kiln no longer has to perform the full calcination function.

Precision: The measure of agreement among repeated measurements of the same property under identical, or substantially similar conditions; calculated as either the range or as the standard deviation. May also be expressed as a percentage of the mean of the measurements, such as relative range or relative standard deviation (coefficient of variation).

Preheater: An apparatus used to heat the raw mix before it reaches the dry kiln itself. In modern dry kilns, the preheater is commonly combined with a precalciner. Preheaters make use of 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.

Quality assurance (QA): A system of management activities involving planning, implementation, assessment, and reporting to make sure that the end product (for example, environmental data) is of the type and quality needed to meet the needs of the user.

Quality control (QC): Overall system of operational techniques and activities that are used to fulfil requirements for quality.

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

Recovery: Any operation the principal result of which is waste serving a useful purpose by replacing other materials which 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.

Representative sample: A sample of a universe or whole (for example, waste pile) which can be expected to exhibit the average properties of the universe or whole.

Representativeness: A qualitative term that expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

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, which is fed either with a batch or continuous charge consisting of an intimate mix of fuel and raw materials. Generally considered obsolete for cement manufacture. VSK technology is based on a black meal process, which prevents the use of alternative fuels.

Waste (management) hierarchy: List of waste management strategies arranged in order of preference, with waste prevention being the most desirable option and disposal the least preferred approach. Departing from such hierarchy may be necessary for specific waste streams when justified for reasons of, inter alia, technical feasibility, economic viability and environmental protection.

Wastes: 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.

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
BEP	Best Environmental Practice
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
DE	Destruction Efficiency
DRE	Destruction and Removal Efficiency
EA	Environment Agency of England and Wales
EPA	United States Environmental Protection Agency (http://www.epa.gov/)
ESM	Environmentally Sound Management
GTZ	Deutsche Gesellschaft für Technische Zusammenarbeit GmbH (http://www.gtz.de/)
HAP	Hazardous Air Pollutant
ICP	Inductively Coupled Plasma
IOELV	Indicative Occupational Exposure Limit Value
IPPC	Integrated Pollution Prevention and Control
LCA	Life Cycle Assessment
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
RII	Resource-Intensive Industries
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

Contents

1. Introduction

1.1. Cement Industry Overview

1. Cement is a finely ground, non-metallic, inorganic powder, which, when mixed with water forms a paste that sets and hardens. It is the key constituent of concrete, which is the second most consumed material worldwide after water. Cement production involves the heating, calcining and sintering of a carefully proportioned mixture of calcareous and argillaceous materials, usually limestone and clay, to produce cement clinker, which is then cooled and ground with additives such as gypsum (a setting retardant) to make cement. The most widely used production process for Portland cement clinker is the dry process, which is gradually replacing the wet process. The manufacturing process is described in more detail in Annex 1.

2. Cement manufacture is a resource intensive industry. Normally about 1,5 to 1,7 tonnes of raw materials are quarried per tonne of clinker produced. In addition, the manufacturing process of clinker requires substantial energy in order to bring the kilns to temperatures of over 2000 °C. According to CEMBUREAU, the representative organization of the cement industry in Europe, each tonne of cement produced typically requires 60 to 130 kilograms of fuel oil or its equivalent, depending on the cement type and kiln technology employed, and about 105 KWh of electricity (Loréa, 2007). On average, energy costs (in the form of fuel and electricity) represent 40 percent of cement manufacturing costs (European IPPC Bureau, 2009).

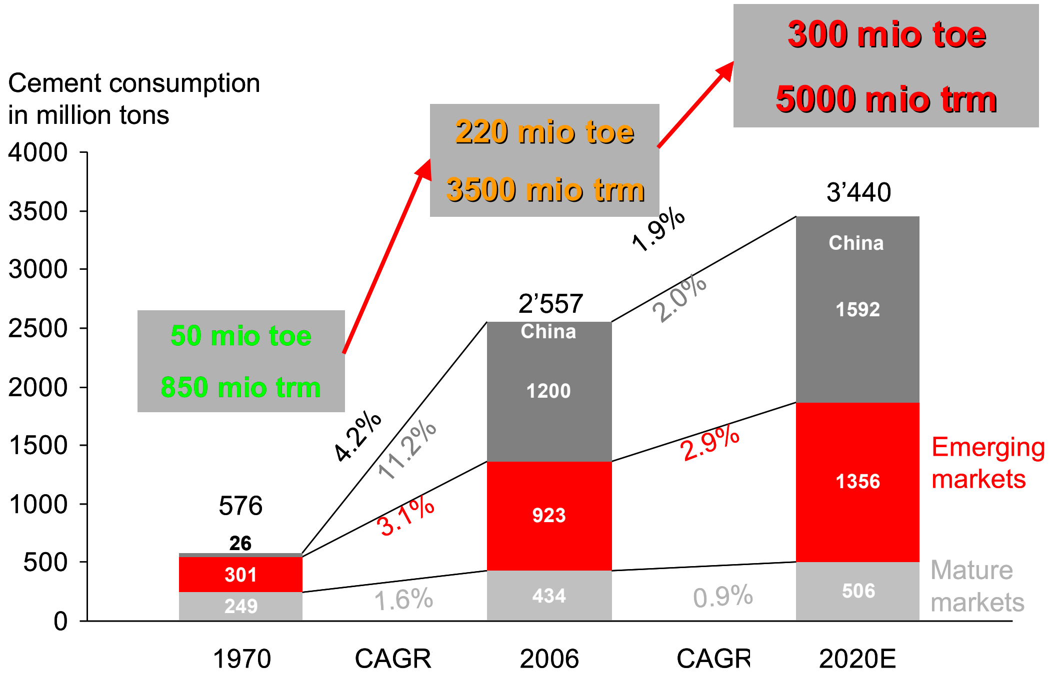
3. In 2008, global cement production was estimated to be 2.9 billion tonnes, with China responsible for about half of the world's production (Da Hai et al., 2009; U.S. Geological Survey, 2009). Consumption of cement is driven primarily by activity in the construction industry, and so is closely linked to the economic cycle. World cement consumption could reach 3,4 billion tonnes by 2020 (Figure 1), with the corresponding increases in energy and raw materials needs.

4. The cement industry has undergone significant consolidation over the past decade through mergers and acquisitions, becoming increasingly characterised by the presence of large, multinational firms. This notwithstanding, it remains a sector with a fairly low global market concentration with the five largest companies accounting for less than 20% of global output[1].

---

[1] According to data obtained from company annual reports: Lafarge (France), Holcim (Switzerland), Cemex (Mexico), Anhui Conch (China), HeidelbergCement (Germany).

Figure 1. Estimated world demand of cement



toe = tons of oil equivalent (42 GJ) ; trm = tons of raw material ; CAGR = Compound annual growth rate

Source: Degré (2009)

5. The clinker burning process is the most important part of the production process in terms of the key environmental issues associated with cement manufacture: energy use and emissions to air. Depending on the specific production processes, cement plants cause emissions to air and waste emissions to land (including cement kiln dust, CKD, where recycling back into the production process may be restricted). In specific rare cases, emissions to water may occur. Additionally, the environment can be affected by noise and odours. The key pollutants released to air are particulates, nitrogen oxides (NO_X) and sulphur dioxide (SO_2) (European IPPC Bureau, 2009). Carbon oxides (CO, CO_2), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCCDs/PCDFs), volatile organic compounds (VOC), metals and their compounds, hydrogen chloride (HCl) and hydrogen fluoride (HF) are emitted as well. Worldwide, cement making is thought to account for 6 percent of the total carbon dioxide (CO_2) emissions from stationary sources (IPCC, 2005). The type and quantity of air emissions depend on different parameters, for example, inputs (the raw materials and fuels used) and the type of process applied. Cement industry operations are also associated with impacts of resource extraction (fossil fuel, limestone, and other minerals) upon environmental quality, biodiversity, and landscape aesthetics; and depletion of non-renewable or slowly renewable resources (fossil fuels or groundwater) (Battelle, 2002).

1.2. Co-processing of Hazardous Waste in the Cement Industry

6. Co-processing in resource-intensive industries (RII) involves the use of 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. In particular, the co-processing of waste materials in cement kilns, the subject of these guidelines, allows the recovery of the energy or mineral value from waste materials, while cement is being produced.

7. Co-processing is a sustainable development concept based on the principles of industrial ecology (Mutz et al., 2007; Karstensen, 2009a), a discipline that focuses on the potential role of industry in reducing environmental burdens throughout the product life-cycle. 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/or raw materials is an example of this type of exchange.

8. In co-processing, wastes serve a useful purpose in replacing part of the materials which would have had to be used for fuel and/or raw materials, thereby conserving natural resources; as such, under the Basel Convention co-processing constitutes an operation "which may lead to resource recovery[2], recycling, reclamation, direct reuse or alternative uses" under R1 ("use as a fuel or other means to generate energy") and/or R5 ("recycling/reclamation of other inorganic materials") of Annex IVB to the Convention.

9. The Basel Convention places obligations on countries that are Parties to ensure environmentally sound management (ESM) of hazardous and other wastes. In this regard, the guiding principle broadly accepted for securing a more sustainable waste management system is the waste hierarchy of management practices which places waste prevention (avoidance) and recovery in a preeminent position relative to disposal. Where waste avoidance is not possible, reuse, recycling and recovery becomes, in many cases, a preferable alternative to final disposal. To this end, co-processing in cement kilns provides an environmentally sound resource recovery option for the management of wastes, preferable to landfilling and incineration.

10. Fossil fuels and raw materials have been successfully substituted by different types of wastes in cement kilns in Europe, Japan, United States, Canada and Australia since the beginning of the 1970s (GTZ/Holcim, 2006). The experience of various jurisdictions with the use of 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.

11. 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, that ensures the complete breakdown of the raw materials into their component oxides and the recombination of the oxides into the clinker minerals. The essential process characteristics for the use of waste can be summarised as follows (European IPPC Bureau, 2009):

- Maximum temperatures of approximately 2000°C (main firing system, flame temperature) in rotary kilns;
- Gas retention times of about 8 seconds at temperatures above 1200°C in rotary kilns;
- Material temperatures of about 1450°C in the sintering zone of rotary kilns;
- Oxidising gas atmosphere in rotary kilns;
- Gas retention time in the secondary firing system of more than 2 seconds at temperatures above 850°C; in the precalciner, the retention times are correspondingly longer and temperatures are higher;
- Solids temperatures of 850°C in the secondary firing system and/or the calciner;

---

[2] In accordance with the European Court of Justice's judgement of 13 February 2003 delivered in case C-458/00.

- Uniform burnout conditions for load fluctuations due to the high temperatures at sufficiently long retention times;
- Destruction of organic pollutants due to the high temperatures at sufficiently long retention times;
- Sorption of gaseous components like HF, HCl, and SO_2 on alkaline reactants;
- High retention capacity for particle-bound heavy metals;
- Short retention times of exhaust gases in the temperature range known to lead to formation of PCDDs/PCDFs;
- Complete utilisation of fuel ashes as clinker components and hence, simultaneous material recycling and energy recovery;
- Product specific wastes are not generated due to a complete material utilisation into the clinker matrix (although some cement plants dispose of CKD or bypass dust);
- Chemical-mineralogical incorporation of non-volatile heavy metals into the clinker matrix.

12. As highlighted by various authors (for example, Mantus, 1992; Battelle, 2002; WBCSD, 2005; Karstensen, 2007b), the utilisation of wastes in the cement industry, principally as alternative fuels but also as supplementary raw materials, has numerous potential benefits, including the recovery of the energy content of waste, conservation of non-renewable fossil fuels, reduction of CO_2 emissions, reduction in production costs, and use of an existing technology to treat hazardous wastes.

13. The embodied energy in alternative fuels that is harnessed by cement plants is the most direct benefit, as it replaces demand for fossil fuels (Murray and Price, 2008). By co-processing waste in a cement kiln and substituting for a non-renewable source, 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.

14. Additionally, the fuel substitutes may have lower carbon contents (on a mass basis) than fossil fuels, and alternative raw materials such as slags or fly ash, that do not require significantly more heat (and hence fuel) to process, may contribute part of the CaO needed to make clinker from a source other than $CaCO_3$ (Van Oss, 2005). Therefore, another direct benefit of waste co-processing is a potential reduction in CO_2 emissions from cement manufacturing. Moreover, through integrating cement kilns within an overall waste management strategy, co-processing may offer a potential to reduce net global CO_2 emissions relative to a scenario in which waste is combusted in an incinerator without energy recovery (EA, 1999b; CEMBUREAU, 2009).

15. The use of alternative materials to replace the traditional raw materials also reduces the exploitation of natural resources and the environmental footprint of such activities (WBCSD, 2005; CEMBUREAU, 2009).

16. In addition to the aforementioned direct advantages of using waste materials for cement manufacturing, there are cost savings derived from the utilisation of pre-existing kiln infrastructure to co-process waste that cannot be minimised or otherwise recycled, thus avoiding the need to invest in purpose-built incinerators or landfill facilities (GTZ/Holcim, 2006; Murray and Price, 2008). Furthermore, unlike with dedicated waste incinerators, when waste materials are co-processed in cement kilns, ash residues are incorporated into the clinker, so there are no end-products that require further management.

17. The above notwithstanding, co-processing of hazardous waste in cement kilns should only be performed if the kiln operates according to the standards of best available techniques, and if certain requirements with respect to input control, process control and emission control are met (as described in later sections of these guidelines). Moreover, an appropriate national legal and regulatory framework within which hazardous waste management activities can be planned and safely carried out should be in place to ensure that the waste is properly handled from the point of generation until its disposal, through the operations of segregation, collection, storage, and transportation. 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 which pertain to the ESM of hazardous wastes.

2. Key Aspects in Co-processing of Hazardous Waste in Cement Kilns

2.1. Principles of Co-processing in the Cement Industry

18. Waste co-processing in cement manufacturing, when carried out in a safe and sound manner, is recognised for far-reaching environmental benefits (CEMBUREAU, 1999a; 2009), however these may be outweighed by poor planning if, for instance, it results in increased pollutant emissions or fails to give priority to a more desirable waste management practice (in terms of the overall environmental outcome). A set of general principles were developed by Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH and Holcim Group Support Ltd. to help avoid the latter scenarios (GTZ/Holcim, 2006). These principles (Table 1) provide a comprehensive yet concise summary of the key considerations for co-processing project planners and stakeholders. The World Business Council for Sustainable Development (WBCSD, 2005) has also outlined similar principles, while Karstensen (2008a, 2009a) has laid out a series of general requirements specific to cement kilns co-processing hazardous wastes on a routine basis. The latter were adopted by the South African Government Department of Environmental Affairs and Tourism (2009) in the framework within which the co-processing in cement production shall be implemented in that country (see Table 2).

Table 1. General principles for co-processing of wastes in cement kilns

Principle	Description
The waste management hierarchy should be respected	– Waste should be co-processed in cement kilns only if there are not more ecologically and economically better ways of recovery – Co-processing should be considered an integrated part of waste management – Co-processing should be in line with the Basel and Stockholm Conventions and other relevant international environmental agreements
Additional emissions and negative impacts on human health must be avoided	– Negative effects of pollution on the environment and human health must be prevented or kept at a minimum – Air emissions from cement kilns co-processing waste cannot be statistically higher than those not co-processing waste
The quality of the cement must remain unchanged	– The product (clinker, cement, concrete) must not be used as a sink for heavy metals – The product must not have any negative impacts on the environment (for example, as determined by leaching tests) – The quality of the product must allow for end-of-life recovery
Companies that co-process must be qualified	– Assure compliance with all laws and regulations – Have good environmental and safety compliance records – Have personnel, processes, and systems in place committed to protecting the environment, health, and safety – Be capable of controlling inputs to the production process – Maintain good relations with public and other actors in local, national and international waste management schemes

Principle	Description
Implementation of co-processing must consider national circumstances	– Country specific requirements and needs must be reflected in regulations and procedures – A stepwise implementation allows for the build-up of required capacity and the set-up of institutional arrangements – Introduction of co-processing goes along with other change processes in the waste management sector of a country

Source: GTZ/Holcim (2006)

Table 2. General requirements for co-processing of 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) Adequate air pollution control devices and continuous emission monitoring of identified parameters ensuring compliance with regulation and permits;
(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) An environmental management and continuous improvement system certified according to ISO 14001, EMAS or similar internationally accepted standard;
(17) Independent audits, 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: South African Government Department of Environmental Affairs and Tourism (2009)

2.2. Considerations for Selection of Wastes

19. The strict quality controls for cement products and the nature of the manufacturing process mean that only carefully selected waste is suitable for use in co-processing (WBCSD, 2005).

20. Changes in technology and consumer behaviour also mean that co-processing may not always be the most cost-effective or environmentally preferred way of using a waste stream, because of changes in technology and consumer behaviour (WBCSD, 2005). When deciding on the suitability

of a waste stream for co-processing, besides taking into consideration the chemical composition of the final product (cement) and determining whether the use of the waste will result in damage to the environment or public health and safety, it needs to be ascertained that cost-effective higher-order uses of the material, according to the waste management hierarchy, are not available. Life Cycle Assessment (LCA) is a tool that may assist the decision making process by comparing different waste management scenarios.

21. As a basic rule, waste accepted as an alternative fuel and/or raw material should give an added value for the cement kiln in terms of the heating value of the organic part and/or the material value of the mineral part. 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 be dependent upon each plant's ability to handle any particular waste stream. The use of cement kilns as a disposal operation not leading to resource recovery, should only be considered if there are environmental benefits to be gained by the kiln operator (for example, NO_x reduction through flame cooling) or it provides a cost-effective and environmentally sound disposal option at the local level.

22. Due to the heterogeneous nature of waste, blending and mixing of different waste streams may be required to guarantee a homogeneous feedstock that meets specifications for use in a cement kiln. However, blending of hazardous wastes should not be conducted with the aim to lower the concentration of hazardous constituents in order to circumvent regulatory requirements. As a general principle, the mixing of wastes must be prevented from leading to the application of an unsuitable (non-environmentally sound) disposal operation (European IPPC Bureau, 2006).

2.2.1 Wastes suitable for co-processing in cement kilns

23. A wide range of wastes are amenable to co-processing; however, because cement kiln emissions are site-specific, the decision on what type of waste can be finally used in a certain plant cannot be answered uniformly. The selection of wastes is influenced by many factors other than the nature of the waste itself. Consideration needs to be given to kiln operation; raw material and fuel compositions; waste feed points; gas-cleaning process; resulting clinker quality; general environmental impacts; probability of formation and release of persistent organic pollutants (POPs); particular waste management problems; regulatory compliance; and public and government acceptance (Van Oss and Padovani, 2003; GTZ/Holcim, 2006; UNEP, 2007; European IPPC Bureau, 2009).

24. 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. Some of the variables that should be considered when selecting waste materials include (WBCSD, 2005; UNEP, 2007):

(a) Kiln operation:

– Alkali (sodium, potassium, etc.), sulphur and/or chloride content: Excessive inputs of alkalis, sulphur and/or chlorides may lead to 'build-up' and blockages in the kiln system. Where these compounds cannot be further captured in the cement clinker or kiln dust, a bypass may be required to remove excess alkali, chloride and sulphur compounds from preheater/precalciner kiln systems. In addition, high alkali content may limit recycling of CKD to the operation.

– Heating (calorific) value: The heating value is the key parameter for the energy provided to the process.

- Water content: Overall moisture content may affect productivity and efficiency of the kiln system, therefore water content of waste needs to be considered in conjunction with that of conventional fuels and/or raw feed materials.
- Ash content: The ash content affects the chemical composition of the cement and may require an adjustment of the composition of the raw mix.
- Exhaust gas flow rate and waste feed rate, to assure sufficient residence time for destruction of organics and to prevent incomplete combustion due to waste overcharging.
- Stability of operation (for example, duration and frequency of CO trips), and the state (liquid, solid), preparation (shredded, milled) and homogeneity of the waste.

(b) Emissions:

- Sulphur content: Sulphur bearing compounds may result in the release of sulphur oxides.
- Organic content: Organic constituents are associated with emissions of CO_2 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.
- Chloride content: These may combine with alkalis to form fine particulate matter composed of chlorides of those alkalis, which can be difficult to control; in some cases, chlorides have combined with ammonia present in the limestone feed to produce highly visible detached plumes of fine particulate composed mainly of ammonium chloride.
- Metals content: The non-volatile behaviour of the majority of heavy metals means that most pass straight through the kiln system and leave as a constituent of the clinker. Volatile metals introduced into the kiln will be in part internally recycled by evaporation and condensation processes, if not emitted in the exhaust gas of the kiln, and build-up within the kiln system until equilibrium is reached and maintained. Thallium, mercury and their compounds are easily volatilized and to a lesser extent so are cadmium, lead, selenium and their compounds. Dust control devices can only capture the particle-bound fraction of heavy metals, which needs to be taken into account when wastes containing volatile metals are co-processed. Wood treated with copper, chromium, arsenic etc. also requires special consideration with regard to the efficiency of the exhaust gas cleaning system. Mercury is a highly volatile metal that is difficult to capture in air pollution control equipment, so the amount of mercury in the total waste feed to kilns should be limited.
- Alkali bypass exhaust gas: At facilities equipped with an alkali bypass, the alkali bypass gases can be released either from a separate exhaust stack or from the main kiln stack. According to U.S. EPA (1998) it is expected that the same hazardous air pollutants (HAPs) found in the main stack are found in the alkali bypass stack, therefore similar pollution abatement equipment and monitoring is deemed necessary.

(c) Clinker, cement and final product quality:

- Phosphate content: Elevated levels of phosphates may retard setting time.
- Fluorine content: Elevated levels of fluorine affect setting time and strength development.
- Chlorine, sulphur, and alkali content: Elevated levels of alkali, chloride or sulphur compounds may affect overall product quality.

- Thallium and chromium content: These affect cement quality and may cause allergic reactions in sensitive users. The leachability of chromium from concrete debris may be higher than that of other metals (Van der Sloot et al., 2008), however, hexavalent chromium (chromium VI) is a natural constituent of cement and alternative fuels comprise only a minor source (European IPPC Bureau, 2009).
- 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 (aluminium and barium for instance) may approach drinking water standards (GTZ/Holcim, 2006).

25. Generally, only waste of known composition and known energy and/or mineral value is suitable for co-processing in cement kilns. Moreover, plant-specific health and safety concerns need to be addressed as well as due consideration given to the waste management hierarchy (as a general principle). The following wastes are normally not recommended for co-processing in cement kilns:

- Radioactive waste;
- Electric and electronic waste (e-waste);
- Whole batteries;
- Corrosive waste;
- Reactive waste, including explosive waste, cyanide bearing waste and water-reactive waste;
- Mercury waste; and
- Waste of unknown or unpredictable composition, including unsorted municipal waste.

26. Individual facilities may exclude other wastes outside the above list depending on local circumstances. For instance, lack of regulations – and 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, although process conditions in cement kilns would be appropriate to dispose of infectious wastes.

27. Besides health and safety concerns, wastes that are not recommended for co-processing in cement kilns are in general excluded from consideration because of their potentially negative impacts on kiln operation, clinker quality and air emissions, and when an alternative waste management option should be preferred.

28. Cement plants are not designed or operated to meet safety and health requirements for radioactive waste management, for which the preferred approach is concentration (reduction of volume) and containment of radionuclides by means of a conditioning process to prevent or substantially reduce dispersion in the environment.

29. Electric and electronic waste contains valuable resources such as precious metals and recycling should be the preferred option. Co-processing of plastic parts from end-of-life electronics might be an option after appropriate disassembly and sorting.

30. Co-processing of batteries would lead to undesirable concentrations of pollutants in the cement and air emissions. Moreover, batteries contain valuable resources such as lead and recycling should be the preferred waste management option.

31. Corrosive wastes may cause corrosion and fouling problems in equipment not specifically designed for this type of waste. Wastes with high chlorine and sulphur contents, such as some mineral acids, may also have a negative impact on the clinker production process and possibly lead to unwanted emissions or affect product quality.

32. Explosive waste should not be co-processed because explosive reactions in the cement kiln would have a negative impact on process stability. There are also occupational safety concerns due to the risk of uncontrolled explosions during transport and pre-processing activities.

33. The high volatility of mercury in cement kilns poses a problem regarding air emissions. It is generally recommended that wastes that contain more than 10 ppm mercury should not be fed to the kiln.

2.2.2 Waste recovery and final disposal in cement kilns

34. Selected waste streams with recoverable energy value can be used as fuels in a cement kiln, replacing a portion of conventional fuels, if they meet specifications. Similarly, selected waste streams containing useful components such as calcium, silica, alumina, and iron can be used as raw materials in the kiln, replacing raw materials such as clay, shale, and limestone. Some wastes will meet both of these requirements and will be suitable for processing for energy recovery and for materials recovery or as an ingredient.

35. Conversely, waste combustion in a cement kiln without any substitution should be considered to constitute a waste disposal operation not leading to the possibility of resource recovery[3].

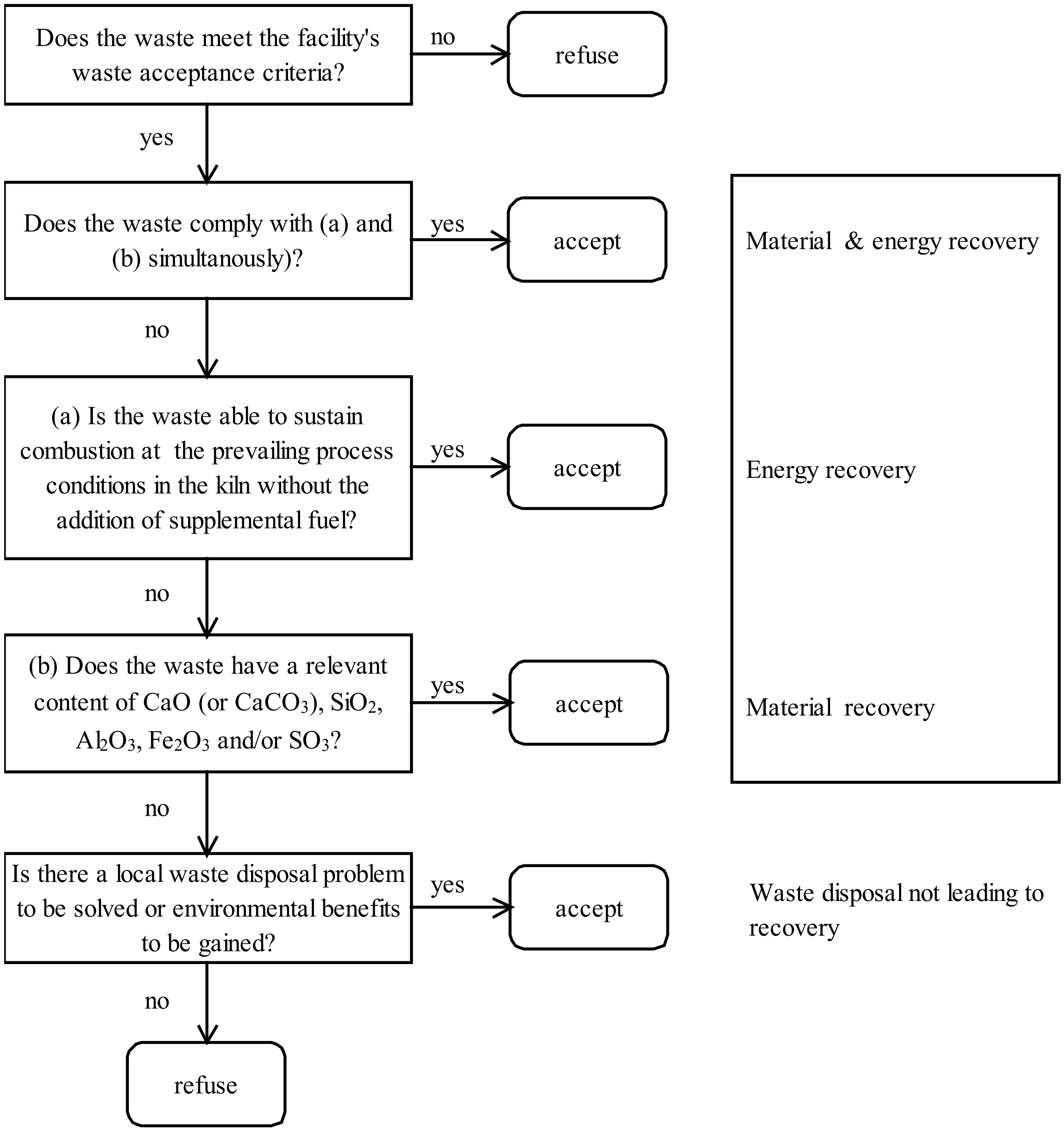
36. To distinguish between operations that lead to resource recovery and those that do not, specific criteria may need to be developed to evaluate the contribution of the waste to the production process. The general decision-making process is outlined in Figure 2. To this respect, some approaches have 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 $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, SO_3, and/or water) to assess its mineral value (Zeevalkink, 1997; Koppejan and Zeevalkink, 2002; GTZ/Holcim, 2006). An example is provided in Annex 2.

37. Although wastes without, for all practical purposes, 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, for the kilns to be used for the disposal of particularly problematic waste streams such as obsolete pesticide stocks. However, this is an activity that is outside the scope of co-processing, and needs to be assessed on a case-by-case basis as well as agreed upon jointly by regulatory authorities and operators. Trial burns may need to be conducted to demonstrate that performance criteria are met.

---

[3] In the European Union the term "disposal" is used to refer to disposal operations listed in Annex IV.A of the Basel Convention (operations which do not lead to the possibility of resource recovery) and "recovery" for operations listed in Annex IV.B (operations which may lead to resource recovery). In the Basel Convention itself, however, the term "disposal" is used to refer to operations listed in both Annex IV.A and Annex IV.B.

Figure 2. Waste acceptance decision process



2.2.3 Trial burns

38. Trial burns are recommended to demonstrate destruction of wastes consisting of, containing or contaminated with POPs. To verify the ability of a facility to efficiently destroy organic pollutants in an irreversible and sound way, the destruction and removal efficiency (DRE) or destruction efficiency (DE) should be determined, as demonstrated in a trial burn. The trial burn involves selecting a principal organic hazardous constituent (POHC) in the waste feed, and sampling and analysis to determine input and emission rates of the same POHC. A trial burn typically consists of a series of tests (one for each set of operating conditions for which the facility desires to be permitted), and there are usually three runs performed for each test.

39. Trial burns with hazardous wastes require professional supervision and independent verification (Karstensen, 2008a). Prior to a trial burn, the operator should demonstrate to the satisfaction of the competent authorities that the baseline operation is properly controlled and that there are safeguards against potential environmentally damaging abnormal operations. To this end it is recommended that the general requirements set out in Table 2 be thoroughly considered.

40. During the trial burn, operating limits are established for parameters that may adversely affect the attainment of the demonstrated DRE or DE during routine operations, namely maximum hazardous waste feed and maximum kiln production rate (Karstensen, 2009b). Subsequent to the trial burn, permit limits are established for these parameters.

41. A cement kiln should demonstrate that it is capable of destroying (through combustion) or removing (through settling in ductwork or capture in air pollution control devices) at least 99.9999 percent of targeted POPs (for non-POPs contaminants a DRE of 99.99 percent needs to be demonstrated). Moreover, a PCDDs/PCDFs emission limit of 0.1 ng TEQ/Nm^3 [4] should be met under testing conditions (SBC, 2007). The cement kiln should also comply with existing emission limit values.

42. An alternative approach to trial burns under worst-case conditions, that is considered to provide the same qualitative information, has been proposed by Karstensen (2009b). This involves conducting a baseline emissions study (no hazardous waste fed to the kiln) and one test run to obtain destruction performance and pollutant emissions data while feeding hazardous waste into the kiln; both tests conducted under normal operating conditions, all the while meeting an emissions limit for PCDDs/PCDFs of 0.1 ng TEQ/Nm^3 as well as meeting 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 percent for fenobucarb and 99.9999832 percent for fipronil in a cement kiln in Vietnam (Karstensen et al., 2006).

43. A compilation of performance verification and test burns results are provided in Annex 3.

2.3. Quality Assurance/Quality Control

44. A comprehensive quality assurance (QA) and quality control (QC) programme is necessary to ensure that the product meets standard specifications, that plant operations are not negatively affected by the use of hazardous wastes, to protect the environment and to reduce risks to worker health and safety. QA is necessary for ensuring that all data and the decisions based on that data are technically sound, statistically valid, and properly documented.

45. 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 encompass all materials handled at the facility (waste streams and product), and should give detailed instructions for the following:

- Organization and responsibilities;
- QA objectives for measurement data in terms of precision, accuracy, completeness, representativeness, and comparability;

---

[4] Dry basis, corrected to 11 percent O_2, 101.3 kPa and 273.15 K.

- Sampling procedures;
- Sample handling and custody;
- Analytical procedures;
- QC checks (blanks, spikes, replicates, etc.) and frequency;
- Instrument/equipment testing, inspection, or maintenance;
- Instrument/equipment calibration procedures and frequency; and
- Data review, verification, validation, and reporting.

46. Adequate laboratory design, infrastructure, equipment, and instrumentation should be provided and maintained to ensure that all required analysis are completed in a timely manner. Periodic interlaboratory tests should be considered in order to evaluate and improve laboratory performance.

47. Safety and health considerations should be taken into consideration when conducting sampling. Employees who perform sampling activities should be properly trained with respect to the hazards associated with waste materials, as well as with any waste handling procedures that will assist in protecting the health and safety of the sampler. In addition, the employees should be trained in the proper protective clothing and equipment that must be used when performing sampling activities. All persons involved in sampling activities should be fully aware of applicable QA/QC procedures.

48. As regards best available techniques (BAT) for waste quality control in the cement industry, the following have been identified by the European IPPC Bureau (2009):

- 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;
- 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; and
- To apply QA systems for each waste load.

49. Internal audits should be carried out with sufficient frequency to ensure that QA/QC procedures are in use and to ensure that personnel conform to these procedures. Independent third party audits should be conducted at least once a year or as required to determine the effectiveness of the implemented quality system. Audit reports should be submitted to management with requirements for a plan to correct observed deficiencies.

2.4. Health and Safety Aspects

50. The protection of health and safety during hazardous waste activities should be integrated into all aspects of facility operations, and should be a conscious priority for all involved, from corporate management to the most recently hired employee. Overall and specific personnel requirements, the chain of command, and individual roles and responsibilities, should be clearly established.

51. 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.

52. Adequate documentation and information on safe hazardous waste handling, operating procedures and emergency contingency measures are mandatory. Facility management staff must ensure an informed workforce through openness and transparency about health and safety measures and standards. Safety and emergency instructions must be provided to employees and contractors in due time, and should be easily understandable.

2.4.1 Hazard analysis

53. The hazards and potential exposures affecting facility employees should be determined to ensure that appropriate control practices and techniques are in place to maintain worker health and safety, and identify hazards present that would require the use of personal protective equipment (PPE). To this end, techniques 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.

2.4.2 Access and hazard control

54. To eliminate or control worker exposure to hazards, the following should be considered (in order of preference):

- Engineering controls, to preclude worker exposure by removing or isolating the hazard (for example, ventilation or use of remotely operated material handling equipment);
- Administrative controls, to manage worker access to hazards or establish safe work procedures (for example, security measures to prevent unauthorized or unprotected access to hazardous wastes on-site); and
- PPE, when engineering or administrative controls are not feasible or do not totally eliminate the hazard.

55. An appropriate combination of the above should be used to reduce and maintain employee exposure to or below national occupational exposure limit values, or, if these are not available, below published exposure levels, examples of which include: the Threshold Limit Value (TLV) occupational exposure guidelines published by American Conference of Governmental Industrial Hygienists (ACGIH); the Pocket Guide to Chemical Hazards published by the United States National Institute for Occupational Health and Safety (NIOSH); Permissible Exposure Limits (PELs) published by the Occupational Safety and Health Administration of the United States (OSHA); Indicative Occupational Exposure Limit Values (IOELVs) published by European Union member states, or other similar sources.

56. For hazardous substances and health hazards for which there is no permissible exposure limit or published exposure limit, the operator should use the published literature and material safety data sheets (MSDS) as a guide in making the determination as to what level of protection is appropriate.

2.4.3 Personal protective equipment

57. Employees, contractors and individuals visiting the installation, should be provided with and required to use PPE where engineering control methods are infeasible to reduce exposure to or below the permissible exposure limits. PPE should be selected to protect against any hazard that is present or likely to be present and should be appropriate to the task-specific conditions and duration.

58. An explanation of equipment selection and use, maintenance and storage, decontamination and disposal, training and proper fit, donning and doffing procedures, inspection, in-use monitoring, program evaluation, and equipment limitations, should be provided to all personnel involved in hazardous waste operations.

2.4.4 Training

59. Effective training is one of the most important keys to worker safety and health. Employees should be trained to a level required by their job function and responsibility before they are permitted to engage in hazardous waste operations that could expose them to hazardous substances, safety, or health hazards. Training activities should be adequately monitored and documented (curriculum, duration, and participants).

60. The training should cover safety, health and other hazards present on the facility; use of personal protective equipment; work practices by which the employee can minimize risks from hazards; safe use of engineering controls and equipment on the site; and, medical surveillance requirements including recognition of symptoms and signs which might indicate over exposure to hazards. Employees who are engaged in responding to hazardous emergency situations should also be trained in how to respond to such expected emergencies.

2.4.5 Medical surveillance

61. A medical monitoring programme should be implemented to assess and monitor employee health both prior to employment and during the course of work, to provide emergency and other treatment as needed. An effective programme should consider at least the following components:

- Pre-employment screening, to determine fitness-for-duty, including the ability to work while wearing PPE, and provide baseline data for future exposures;
- Periodic medical monitoring examinations (the content and frequency of which would depend on the nature of the work and exposure), to determine biological trends that may mark early signs of chronic adverse health effects; and
- Provisions for emergency treatment and acute non-emergency treatment.

2.4.6 Emergency response

62. Emergency preparedness should be established for the protection of the workforce and public before hazardous waste operations can begin. An Emergency Response Plan should be in place to ensure that appropriate measures are taken to handle possible on-site emergencies and coordinate off-site response. At minimum, this plan should address the following:

- Pre-emergency planning and coordination with outside emergency responders;
- Personnel roles, lines of authority, training and communication procedures;

- Emergency recognition and prevention procedures;
- Safe distances and places of refuge;
- Site security and control procedures;
- Evacuation routes and procedures;
- Site mapping highlighting hazardous areas, site terrain, site accessibility and off-site populations or environments at potential risk;
- Decontamination procedures;
- Emergency medical treatment and first aid procedures;
- Personal protective and emergency equipment at the facility;
- Emergency alerting and response procedures;
- Documenting and reporting to local authorities; and
- Critique of response and follow-up procedures.

63. 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 the hazardous waste storage and processing areas.

64. The Plan requirements should be rehearsed regularly using drills and mock situations, and reviewed periodically in response to new or changing facility conditions or information.

65. 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.

2.5. Communications and Stakeholder Involvement

66. Stakeholders are all the individuals and groups who see themselves as potentially affected by the operations of a facility, whether on a local, national, or international scale. These include, but are not limited to, neighbours, community organizations, employees, trade unions, government agencies, the media, non-governmental organizations (NGOs), contractors, suppliers, and investors.

67. Public communication means providing information through any media, including brochures, websites, newspapers, radio and television. Stakeholder involvement means listening directly to community members and others with an interest in the facility, through public meetings, presentations, advisory committees, and personal conversations.

68. Communication and stakeholder involvement should occur as part of the normal operations of a plant. Facilities need to be clear about their objectives for working with stakeholders, have a reasonable timescale for engagement, commit the necessary resources, and be prepared to work with stakeholders to find mutually beneficial outcomes. Detail on how to design and develop a communications and stakeholder involvement plan is provided by U.S. EPA (1996), Hund et al. (2002), and The Environment Council (2007), among others.

69. Operators and regulatory authorities should be prepared to address public concerns over possible impacts of co-processing, and they should strive to establish efficient communication processes in order to explain the activities. Operators planning to handle and/or co-process hazardous waste should provide all necessary information to allow stakeholders to understand the purpose of the use of such wastes in the cement kiln, and to make them aware of the measures that will be implemented to avoid adverse impacts on the public and the environment.

3. Waste Acceptance and Pre-processing

3.1. Introduction

70. Due to the heterogeneous nature of waste, co-processing in cement kilns generally requires some degree of waste processing to produce a relatively uniform waste stream that complies with the technical and administrative requirements of cement manufacture and to guarantee that environmental standards are met[5]. However in some instances, as is for example the case of used oil or tyres, wastes may be used 'as-delivered' and without further processing.

71. With any process, the quality of what goes in determines the quality of what comes out. Therefore, attention should be paid to the selection of suitable waste materials, whether they are collected directly from the generators or through intermediaries. Operators need to ensure that only hazardous waste originating from trustworthy parties will be accepted (with deliveries of unsuitable wastes refused), considering the integrity of all participants throughout the supply chain. Only qualified, authorized and licensed transport companies should be used, otherwise, serious accidents and incidents may arise due to incompatible, poorly labelled or poorly characterised wastes being mixed or stored together.

72. The following recommendations provide only general indications on the management of wastes, in particular hazardous wastes. Specific handling requirements shall need to 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.

3.2. Waste Acceptance

73. Knowledge of wastes, before they are accepted and processed, is necessary to enable the operator to ensure that the waste is within the requirements of the facility's permit and will not adversely affect the process. Generators of hazardous waste should, in most circumstances, be best placed to know the composition, nature and problems associated with their waste and should ensure that all information concerning it is passed to those involved in its subsequent management. However, sometimes the generator of the waste may wrongly consider a waste as non-hazardous, or the constituent present at greatest concentration may be used to describe the waste although this may not be the constituent which has the potential to be most hazardous or cause most harm.

74. Waste acceptance comprises two stages: pre-acceptance (or screening) and on-site acceptance. Pre-acceptance involves the provision, as necessary, of information and representative samples of the waste to allow operators to determine the suitability of the waste before arrangements are in place to accept the waste. The second stage involves acceptance procedures when the waste arrives at the facility to confirm the characteristics of waste previously approved.

75. Failure to adequately screen waste samples prior to acceptance and to confirm its composition on arrival at the installation may lead to subsequent problems, including an inappropriate storage and mixing of incompatible substances, and accumulation of wastes.

---

[5] 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.

3.2.1 Pre-acceptance

76. A pre-acceptance (or pre-shipment screening) protocol should be designed to ensure that only hazardous waste streams that can be properly and safely handled are approved for shipment to the facility. Such protocol is necessary to:

- Ensure regulatory compliance by screening out unsuitable wastes;
- Confirm the details relating to composition, and identify verification parameters that can be used to test waste arriving at the facility;
- Identify any substances within the waste that may affect its processing, or react with other reagents; and
- Accurately define the range of hazards exhibited by the waste.

77. The operator should obtain information on the nature of the process producing the waste, including the variability of this process; an appropriate description of the waste regarding its composition (chemicals present and individual concentrations), handling requirements and associated hazards; the quantity of waste; the form the waste takes (solid, liquid, sludge etc); and, sample storage and preservation techniques. Where possible, the information should be provided by waste generators themselves, otherwise a system for the verification of the information provided by any intermediaries should be considered.

78. A system for the provision and analysis of a representative sample(s) of the waste should be in place. The waste sample should be taken by a person who is technically competent to undertake the sampling process, and analysis should be carried out by a laboratory (preferably accredited) with robust QA/QC methods and record keeping; a chain-of-custody procedure should be considered. The operator should ensure that, for each new waste, a comprehensive characterisation (profiling) and testing with respect to the planned processing, is undertaken. No wastes should be accepted at the facility without sampling and testing being carried out, with the exception of unused, outdated or off-specification products which have not been subsequently contaminated (and for which appropriate MSDS or product data sheets are available).

79. A Waste Analysis Plan (WAP) should be prepared and maintained documenting the procedures that should be used to obtain a representative sample of a waste and to conduct a detailed chemical and physical analysis of this representative sample. A WAP should address measures to identify potentially reactive, and incompatible wastes[6]. The WAP should comprise testing of a representative sample of waste to qualify it for use at the facility (for waste pre-acceptance purposes); testing of incoming waste shipments to verify its constituents (for waste acceptance purposes); and testing of samples taken during or after waste pre-processing or blending to verify the quality of the resultant stream.

80. Operators should ensure that the technical appraisal is carried out by suitably qualified and experienced staff who understand the capabilities of the facility.

81. Records relating to the pre-acceptance should be maintained at the facility for cross-referencing and verification at the waste acceptance stage. The information should be recorded and referenced to the waste stream so that it is available at all times. The information must be regularly reviewed and kept up to date with any changes to the waste stream.

---

[6] The U.S. 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.

3.2.2 On-site acceptance

82. On-site verification and testing should take place to confirm the characteristics of the waste, and the consistency with the pre-acceptance information. Acceptance procedures should address:

- Measures to deal with pre-approved wastes arriving on-site, such as a pre-booking system to ensure that sufficient capacity is available;
- Vehicle waiting and traffic control;
- Procedures for checking paperwork arriving with the load;
- Procedures for load inspection, sampling and testing;
- Criteria for the rejection of wastes and the reporting of all non-conformances;
- Record keeping; and
- Procedures for periodic review of pre-acceptance information.

83. Wastes should not be accepted without detailed written information identifying the source, composition and hazard of the waste.

84. Where facilities provide a service to emergency services such as the removal of spillages or fly-tipped hazardous wastes, there may be situations where the operator is unable to adhere to established pre-acceptance and/or acceptance procedures. In such instances, the operator should communicate the occurrence to the competent authorities immediately.

Arrival

85. Hazardous wastes should be received under the supervision of a suitably qualified and trained person, and only if sufficient storage capacity exists and the site is adequately manned. All wastes received at the facility should initially be treated as being unknown and hazardous until compliance with specifications has been positively verified.

86. Waste delivery should accompanied by a suitable description of the waste, including name and address of the generator; name and address of the transporter; waste classification/description; volume/weight; and hazard(s) of the waste (such as, flammability, reactivity, toxicity or corrosivity). Documentation accompanying the shipment should be reviewed and approved (including the hazardous waste manifest documentation, if applicable), and any discrepancies should be resolved before the waste is accepted. If discrepancies cannot be resolved, the shipment should be rejected back to the original generator, or at his request, to an alternate facility.

87. Where possible, waste loads should be visually inspected. Containers should be checked to confirm quantities against accompanying paperwork. Containers should be clearly labelled in accordance with applicable regulations for the transport of dangerous goods and should be equipped with well-fitting lids, caps and valves secure and in place. Drums and containers should be inspected for leaks, holes, and rust. Any damaged, corroded or unlabelled drum should be classified as ‘non-conforming’ and dealt with appropriately.

88. All incoming loads should be weighed, unless alternative reliable volumetric systems linked to specific gravity data are available.

Inspection

89. Wastes should not be accepted at the facility without thorough inspection being carried out. Reliance solely on written information supplied should not be acceptable, and physical verification and analytical confirmation should be required, to the extent necessary to verify that it meets permit specifications and regulatory requirements. All wastes, whether for processing or simply storage, should be sampled and undergo verification and testing, according to the frequency and protocol defined in the WAP (except unused, outdated or off-specification products which have not been subsequently contaminated).

90. On-site verification and testing should take place to confirm:

- The identity and description of the waste;
- Consistency with pre-acceptance information; and
- Compliance with the facility permit.

91. 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)

92. The facility should have a designated sampling or reception area. Containerised waste should be unloaded in this area, only if adequate space is available, and temporarily stored pending further inspection (sampling and sample analysis); wastes should be segregated immediately to remove possible hazards due to incompatibility. Sampling should be performed at the earliest possible time, preferably no later than 24 hours after unloading. During this period, wastes should not be bulked, blended or otherwise mixed. Bulk wastes should be inspected and accepted for processing prior to unloading.

93. Sampling should comply with specific national legislation, where it exists, or with international standards. Sampling should be directly supervised by laboratory staff, and in countries where regulations do not exist, qualified staff should be appointed. Sampling procedures 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/or 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 at the installation.

94. 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 the speed required by facility procedures, which, particularly for hazardous wastes, often means that the laboratory needs to be on-site.

95. Typically, waste shipments are sampled and analyzed for a few key chemical and physical parameters (fingerprint analysis) to substantiate the waste composition designated on the accompanying paperwork (manifest and/or other shipping paper). The selection of key parameters must be based on sufficient waste profile knowledge and testing data to ensure accurate waste representation. When selecting fingerprint parameters, consideration should be given to those parameters that can be used to: identify wastes that are not permitted; determine whether the wastes are within the facility's operational acceptance limits; identify the potential reactivity or incompatibility of the wastes; and indicate any changes in waste composition that may have

occurred during transportation or storage. Should the results of the fingerprint testing 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 when waste can be managed by the facility. Re-evaluation should consider facility conditions for storage and processing; additional parameter analyses performed as deemed appropriate by the operator (and established in the WAP); and permit requirements.

96. The inspection scheme may include (Karstensen, 2008a): 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.

97. Wastes should be moved to the storage area only after its acceptance. Should the inspection or analysis indicate that the wastes fail to meet the acceptance criteria (including damaged or unlabelled drums), then such loads should be stored in a dedicated area allocated for non-conforming waste storage (quarantine area), and dealt with appropriately.

98. 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 made available.

99. Suitable provisions, in accordance with national legislation and practice, should be made to verify that wastes being received at the facility are not radioactive. Plastic scintillation detectors are one type of detector used.

100. After being accepted for processing, hazardous containerised waste should be labelled with the date of arrival on-site and primary hazard class. Where containers are bulked, the earliest date of arrival of the bulked wastes should be transposed from the original container onto the bulk container. A unique reference number should be applied to each container for the purpose of the in-plant waste tracking system.

3.2.3 Non-conforming waste

101. 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), together with a written procedure for tracking and reporting such non-conformance. This should include notification to the customer/waste generator and competent authorities.

102. The operator should also have a clear and unambiguous policy for the subsequent storage (including a maximum storage volume) and disposal of such rejected wastes. This policy should achieve the following:

- Identify the hazards posed by the rejected wastes;
- Label rejected wastes with all information necessary to allow proper storage and segregation arrangements to be put in place; and
- Segregate and store rejected wastes safely pending removal within a reasonable time (where possible, no more than five working days).

103. Wastes that do not fulfil 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.

3.2.4 In-plant tracking system

104. An internal tracking system and stock control procedure should be in place for all wastes, beginning at the pre-acceptance stage, to guarantee the traceability of waste processing and to enable the operator to:

- Prepare the most appropriate waste blend;
- Prevent unwanted or unexpected reactions;
- Ensure that the emissions are either prevented or reduced; and
- Manage the throughput of wastes.

105. The tracking system (which may be a paper system, an electronic system, or a combination of both), should ‘follow’ the waste during its acceptance, storage, processing and removal off-site. It should consequently be possible at any time for the operator to identify where a specific waste is on the facility, and the length of time it has been there. Records should be held in an area well removed from hazardous activities to ensure their accessibility during any emergency.

106. Once a waste has entered bulk storage or a treatment process, the tracking of 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 tank, storage pit or other enclosure. For example, it is necessary to keep track of residues that will be building up within a vessel between de-sludging events in order to avoid any incompatibility with incoming wastes.

107. For bulk liquid wastes, stock control would involve maintaining a record of the route through the process, whereas drummed waste control should utilise the individual labelling of each drum to record the location and duration of storage.

108. The in-plant waste tracking system should hold all the information generated during pre-acceptance, acceptance, storage, processing and removal off-site. Records should be made and kept up to date on an ongoing basis 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 unique reference number;
- Details of the waste generator and intermediate holders;
- Date of arrival on-site;
- Pre-acceptance and acceptance analysis results;
- Container type and size;
- Nature and quantity of wastes held on-site, including identification of associated hazards;
- Details on where the waste is physically located; and
- Identification of staff who have taken any decisions on acceptance or rejection of wastes.

109. The system adopted should be capable of reporting on all of the following:

- Total quantity of waste present on-site at any one time, in appropriate units;
- Breakdown of waste quantities being stored pending on-site processing;

- Breakdown of waste quantities on-site for storage only, that is, awaiting onward transfer;
- Breakdown of waste quantities by hazard classification;
- Indication of where the waste is located relative to a site plan;
- Comparison of the quantity on-site against total permitted; and
- Comparison of time the waste has been on-site against permitted limit.

3.3. Waste Storage and Handling

110. Once it has been determined that the waste is suitable for the installation, the operator should have in place systems and procedures to ensure that wastes are transferred to appropriate storage safely.

111. The issues for the operator to address in relation to measures for waste storage on the installation should include the following:

- Location of storage areas;
- Storage area infrastructure;
- Condition of tanks, drums, vessels and other containers;
- Stock control;
- Segregated storage;
- Site security; and
- Fire risk.

3.3.1 Design considerations

112. Transfer and storage areas should be designed to control accidental spills. This may require that:

- Adequately bunded and sealed storage areas, which are impermeable and resistant to the stored materials, should be provided to prevent spills from spreading and seeping into the soil;
- All spills should be collected, placed in a suitable container, and stored for disposal in the kiln;
- Incompatible wastes should be prevented from mixing in case of a spill;
- All connections between tanks should be capable of being closed via valves, and overflow pipes should be directed to a contained drainage system (that is, the relevant bunded area or another vessel);
- Leak free equipment and fittings should be installed whenever possible;
- Measures to detect leaks and take appropriate corrective action should be provided;

- Contaminated runoff should be prevented from entering storm drains and water courses (any such runoff should be collected and stored for disposal in the kiln); and
- Adequate alarms for abnormal conditions should be provided.

113. Storage design should be appropriate to maintain the quality of the wastes during the storage time. Segregated storage is necessary 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.

114. Storage characteristics should consider the properties of the waste that poses greater risk that can be accepted at specific storage areas within the facility. In general, the storage of wastes needs, additionally, to 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

115. Containerised wastes should be stored under cover, protected from heat and direct sunlight, unless the waste is known to be unaffected by ambient conditions (sunlight, temperature, rain).

116. The design should prevent accumulation of hazardous wastes beyond the allowable period of time in the case of containerised wastes and should consider mixing or agitation to prevent settling of solids in the case of liquid wastes. 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.

117. Tanks, pipelines, valves, and seals must be adapted to the waste characteristics in terms of construction, material selection, and design. They must be sufficiently corrosion proof, and offer the option of cleaning and sampling.

118. Adequate ventilation should be provided in consideration to applicable work exposure guidelines (periodic monitoring for VOC emissions should be considered for open stored wastes that may emit VOC).

119. A fire protection system that meets all standards and specifications from local authorities (for example, local fire department) should be provided. 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 in case of temperature variations.

120. Automatic fire suppression systems should be used in some cases, most commonly when storing flammable liquid waste although also 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, and dry powder systems are commonly used.

3.3.2 Operational considerations

121. There should be written procedures and instructions in place for the unloading, handling, and storage of wastes on-site. It should be ensured that chemical incompatibilities guide the segregation required during storage. Compliance with such procedures should be audited regularly.

122. To avoid the need for additional handling and transfer, a common practice is to ensure, as far as possible, that hazardous wastes are stored in the same containers (drums) that were used to deliver the wastes to the facility.

123. Designated routes for vehicles carrying specific hazardous wastes should be clearly identified within the facility. On-site transportation should be performed in a manner which minimizes 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. 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.

124. Appropriate signs indicating the nature of hazardous wastes should be in place at storage, stockpiling, and tank locations.

125. Containers should be kept in good condition (free of dents, not leaking or bulging), and closed when not removing waste. Container storage areas should be inspected at least weekly.

126. Maintenance work should be authorized by plant management, and carried out once a supervisor has checked the area and necessary precautions have been taken. Special procedures, instructions, and training should be in place for routine operations such as:

- Working at heights, including proper tie-off practices and use of safety harnesses;
- Confined space entry where air quality, explosive mixtures, dust, or other hazards may be present;
- Electrical lock-out, to prevent accidental reactivation of electrical equipment undergoing maintenance; and
- ‘Hot works’ (welding, cutting, etc.) in areas that may contain flammable materials.

127. The following measures should be considered to strengthen safety:

- Storage areas should be kept clear of uncontrolled combustible materials;
- Whenever there is a risk that has not been avoided or controlled by engineering controls or other means, standard safety signs and information signs should be provided;
- Where the eyes or body of any person may be exposed hazardous wastes, emergency showers and eye wash stations should be provided within the work area for immediate emergency use (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);
- Adequate alarms should be provided to alert all personnel about emergency situations;
- Communications equipment should be maintained at the site so that the control room and the local fire department can be contacted immediately in case of a fire; and
- Electrical equipment should be grounded and appropriate anti-static devices selected.

3.4. Waste Pre-processing

128. Wastes used in cement kilns should be homogenous with particle size compatible with the operations involved, and have a stable chemical composition and heat content, so as not to detract from normal kiln operation, product quality, or the site’s normal environmental performance. For optimum operation, kilns require very uniform waste material flows in terms of quality and quantity. For certain types of waste this can only be achieved by its pre-processing.

129. Waste pre-processing can include drying, shredding, grinding or mixing depending on the type of waste, and is usually done in a purpose made facility, which may be located outside or inside the cement plant.

130. Liquid waste fuels are normally prepared by blending different wastes with suitable calorific values and chemistry (like spent solvents or used oil). Normally, only simple pre-treatment is necessary (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.

3.4.1 Design considerations

131. Facility layout should be carefully considered to ensure access for day-to-day operations, emergency escape routes, and maintainability of the plant and equipment.

132. Recognized standards should be applied to the design of installations and equipment. Any modifications should be documented.

133. Operations should be assessed for health and safety risks or concerns to ensure that equipment is safe 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 operability studies.

3.4.2 Operational considerations

134. Mixing and homogenisation of wastes will generally improve feeding and combustion behaviour. Mixing of wastes can involve risks and should be carried out according to a prescribed recipe.

135. Techniques used for waste pre-processing and mixing are wide ranging, and may include:

- Mixing and homogenising of liquid wastes to meet input requirements, for example, viscosity, composition and/or heat content;
- Shredding, crushing, and shearing of packaged wastes and bulky combustible wastes, for example, tyres; and
- Mixing of wastes in a storage pit or similar enclosure using a grab or other machine.

136. Crane operators should be able to identify potentially problematic loads (for example, baled wastes, discrete items that cannot be mixed or will cause loading/feeding problems) and ensure that these are removed, shredded or directly blended (as appropriate) with other wastes.

137. General tidiness and cleanliness contribute to an enhanced working environment and can allow potential operational problems to be identified in advance. The main elements of good housekeeping are:

- The use of systems to identify and locate/store wastes received according to their risks;
- The prevention of dust emissions from operating equipment;
- Effective wastewater management; and
- Effective preventive maintenance.

3.5. Pre-processing Plant Closure/Decommissioning

138. Closure is the period directly after the facility stops its 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.

139. Operators should be required to 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 that the facility is properly closed, a closure plan should be prepared identifying the steps necessary to partially or completely close de facility, including:

- Procedures for handling removed inventory;
- Procedures for decontamination and/or disposal;
- Procedures to confirm effectiveness of decontamination, demolition and/or excavation (including procedures for performing sample collection and analysis);
- Health and safety plan addressing all health and safety concerns pertinent to closure activities; and
- Security system to prevent unauthorized access to the areas affected by closure activities.

140. 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 human health and the environment.

141. To minimise decommissioning problems and associated environmental impacts, the European IPPC Bureau (2006) recommends for existing installations where potential problems are identified, putting in place a programme of design improvements. These designs improvements would need to ensure that underground tanks and piping are avoided (if not possible to replace, then operators should provide secondary containment or develop a suitable monitoring programme), and that there is provision for the draining and clean-out of vessels and piping prior to dismantlement, among others.

3.6. Environmental Aspects

3.6.1 VOC, odours, and dust

142. Emissions to air from waste pre-processing will depend on the types of wastes treated and the processes used. Emission monitoring and reporting must be performed according to locally applicable regulations.

143. Abatement techniques should be in place as needed. Dust is usually reduced by bag filters. Countermeasures for noise and odours should be considered. Common emission control methods for VOC, pending monitoring results, may include biological treatment, activated carbon and thermal treatment, among others.

3.6.2 Drums and ferrous metals

144. Empty drums and ferrous metals removed by magnetic separators should disposed of in accordance with the requirements of local authorities. Metal scrap not containing any contaminants to an extent to render it hazardous can be recycled for steelmaking. Empty drums that formerly contained wastes and are in good condition can be sent to authorised drum washers/recyclers.

3.6.3 Wastewater

145. Discharges of wastewater to surface water should not result in contaminant concentrations in excess of local ambient water quality criteria or, in the absence of local criteria, other sources of ambient water quality. 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.

146. Discharges into public or private wastewater treatment systems should meet the pre-treatment and monitoring requirements of the sewer treatment system into which it discharges, and 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.

3.7. Emissions Monitoring and Reporting

147. Emissions and air quality monitoring programs provide information that can be used to assess the effectiveness of emissions management strategies. A systematic planning process is recommended to ensure that the data collected are adequate for their intended purposes (and to avoid collecting unnecessary data). An air quality monitoring program should consider baseline air quality monitoring at and in the vicinity of the facility to assess background levels of key pollutants.

148. When wastewater is discharged, a wastewater and water quality monitoring program with adequate resources and management oversight should be developed and implemented to meet the objective(s) of the monitoring program.

149. 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 programs 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 conducted by, or under, the supervision of trained

individuals. Analysis should be conducted by entities permitted or certified for this purpose. 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.

4. Co-processing in Cement Kilns

4.1. Introduction

150. For optimal use in cement kilns (co-processing with ‘zero additional emissions’) alternative fuels and raw materials need to be fed to the kiln via appropriate feed points and in adequate proportions, with proper waste quality and emission control systems implemented. The following recommendations are considered to be current best practice within the industry at the time of writing, however the development and introduction of new technologies which meet BAT criteria shall need to be considered.

151. Co-processing has the following characteristics during the production process (GTZ/Holcim, 2006):

- 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 SO_2, HCl, and most of the heavy metals, with the exception of mercury, cadmium and thallium.
- The clinker reactions at 1450°C allow the chemical binding of metals and the incorporation of ashes to the clinker.
- 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 (destruction of organics).

4.2. Operational Requirements

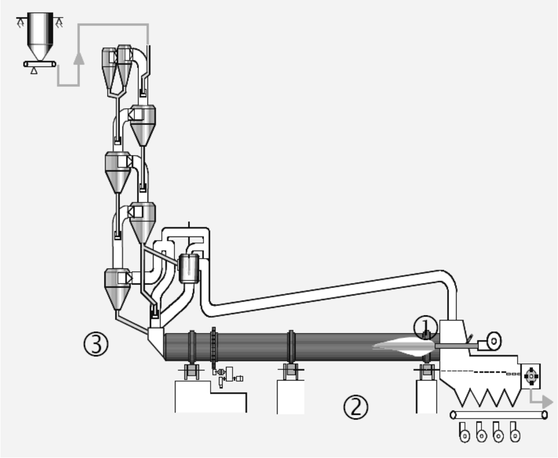
152. Safe and responsible co-processing requires careful selection of the feed points in the kiln system as well as comprehensive operational control according to the specific characteristics and volumes of the waste material.

4.2.1 Feed point selection

153. Many cement kilns co-process waste commercially (that is, they accept waste from off-site generators), in most cases for use as a fuel substitute in the production of cement clinker. Liquid wastes are typically injected into the hot end of the kiln. Solid wastes may be introduced into the calcining zone at some facilities. For long kilns, this means that the solid waste is introduced mid-kiln, and for preheater/precalciner kilns that it is introduced onto the feed shelf in the high-temperature section.

154. In the case of hazardous wastes, complete destruction of combustible toxic compounds such as halogenated organic substances has to be ensured through proper temperature and residence time. In general, waste should be fed through either the main burner or the secondary burner for preheater/precalciner kilns. In the main burner conditions will always be favourable. For the secondary burner it should be ensured that the combustion zone temperature is maintained over 850°C for a sufficient residence time (two seconds).

Figure 3: Temperatures and residence times during cement production

Characteristics	Temperature and time	
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)	
Residence time at precalciner	> 2-6 seconds > 800°C	

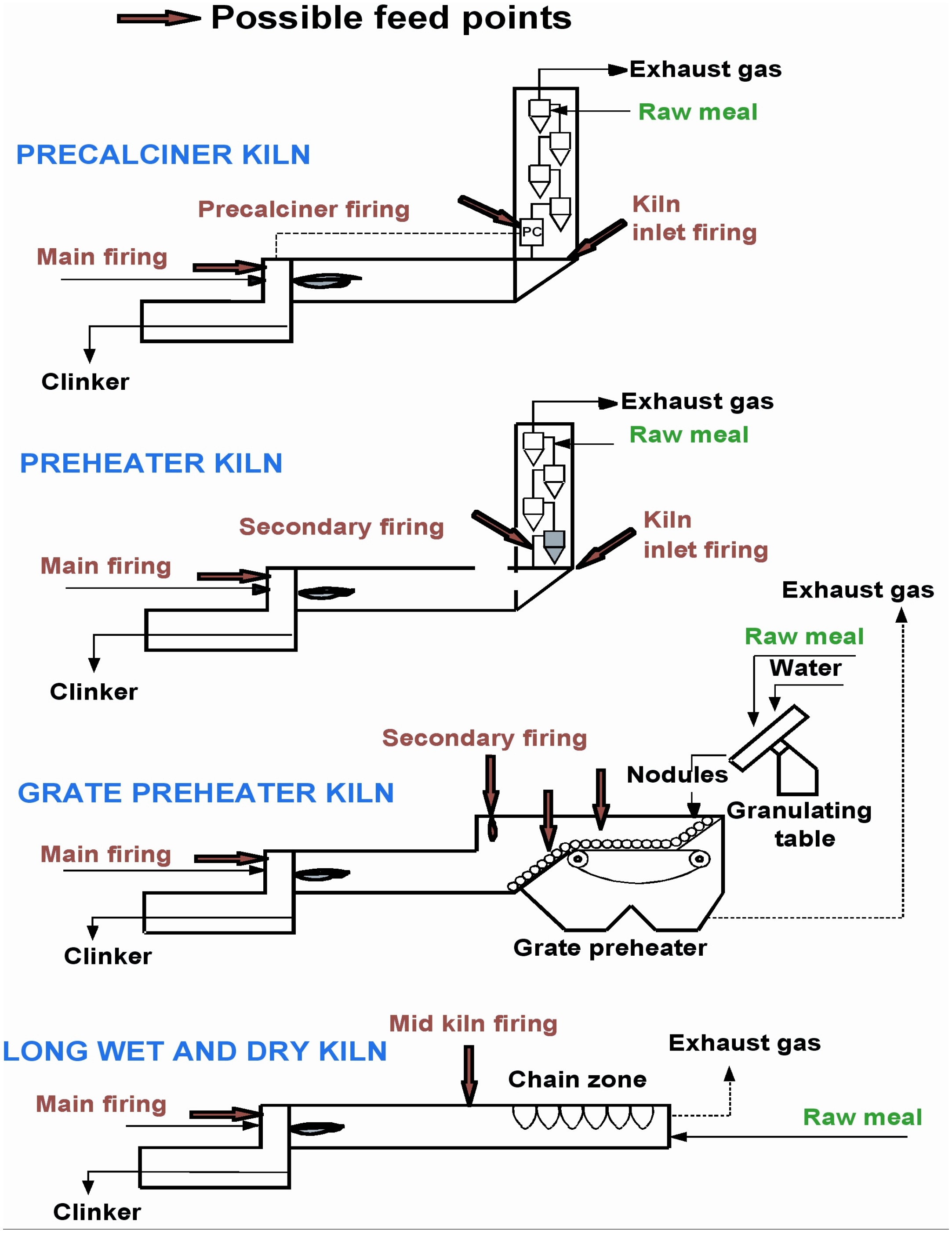
155. If hazardous waste with a content of more than 1 percent of halogenated organic substances (expressed as chlorine) is fed to the kiln, the temperature should be maintained at 1100°C for at least two seconds.

156. Alternative raw materials are typically fed to the kiln system in the same way as traditional raw materials, for example, via the normal raw meal supply. Alternative raw 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. Alternative raw materials containing volatile (organic and inorganic) components should not be fed to the kiln via the normal raw meal supply unless it has been demonstrated by controlled test runs in the kiln or by adequate laboratory tests that undesired stack emissions can be avoided.

157. Adequate feed points should be selected according to the physical, chemical, and (if relevant) toxicological characteristics of the waste material used (see Figure 4). Different feed points can be used to introduce waste materials into the cement production process. The most common ones being:

- Via the main burner at the rotary kiln outlet end;
- Via a feed chute at the transition chamber at the rotary kiln inlet end (for lump fuel);
- Via secondary burners to the riser duct;
- Via precalciner burners to the precalciner;
- Via a feed chute to the precalciner (for lump fuel); and
- Via a mid kiln valve in the case of long wet and dry kilns (for lump fuel).

Figure 4. Typical waste feed points



4.2.2 Kiln operation control

158. The impact of waste materials on the total input of circulating volatile elements such as chlorine, sulphur, or alkalis should be assessed very carefully prior to acceptance, as they may cause operational troubles in a kiln. Specific acceptance criteria for these components should be set by each facility based on the process type and on the specific kiln conditions.

159. The general principles of good operational control of the kiln system using conventional fuels and raw materials should be applied. In particular, all relevant process parameters should be measured, recorded, and evaluated continuously. Kiln operators should be trained accordingly, with special focus on requirements related to the use of waste materials - including health, safety, and environmental emission aspects.

160. Waste should never be fed during start-up and shut-down of the kiln, except nonhazardous waste used as alternative fuel and with combustion characteristics comparable to fossil fuel. For upset conditions of the kiln, written work instructions describing the strategy to disconnect the waste feed to ensure minimum operational stability conditions should be available and known to the kiln operators.

161. The mineral content of the waste may change the characteristics of the clinker. The raw mix composition should be adjusted accordingly to stick 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 alkalis, sulphur and chlorine enrichment cycles should only be considered if appropriate solutions for the management of the bypass dust generated have been identified.

4.3. Environmental Aspects

4.3.1 Air emissions

162. The main emissions from cement kiln systems are emissions to air, whether alternative fuels and/or raw materials are being used or not. Emissions that have been identified as relevant are dust (particulate matter), NOx and other nitrogen compounds, CO, CO_2, SO_2 and other oxides of sulphur, metals and their compounds, HCl, HF, PCDDs, PCDFs, and total organic compounds (TOC) (European IPPC Bureau, 2009). More specifically, emissions may include, inter alia, ammonia (NH_3), benzene, toluene, xylene, polycyclic aromatic hydrocarbons (PAH), chlorobenzenes and PCBs (SBC, 2007). The sources of these emissions are outlined in Annex 4.

163. Existing and potential control technologies are described by Greer (2003) and Karstensen (2008b), while details on BAT are provided by the European IPPC Bureau (2009). The prevention or minimization of the formation and subsequent release of unintentional POPs from cement kilns co-processing hazardous waste is the subject of Article 5 of the Stockholm Convention. Guidance on applicable best available techniques and best environmental practices (BEP) is provided in the "Guidelines on Best Available Techniques and Provisional Guidance on Best Environmental Practices Relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants", which were finalized by the Stockholm Convention Expert Group on Best Available Techniques and Best Environmental Practices in December 2006.

164. For information purposes, emission limits for cement kilns co-processing hazardous wastes are provided in Annex 5. 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.

4.3.2 Cement kiln and bypass dust

165. All cement plants generate a fine dust from the kiln line, collectively labelled CKD. CKD composition varies among plants and 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 consists of fully calcined kiln feed material.

166. The majority of CKD and bypass dust is recycled directly back to the cement kiln and/or cement clinker grinder, thus avoiding disposal. However, some dust may need to be periodically 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. CKD is frequently used for beneficial agricultural applications.

167. To ensure the protection of public health and the environment, discarded bypass dust or CKD from facilities using hazardous wastes as supplementary fuels or raw materials, should be analyzed for leachate (metals and organics) if they are to be land disposed, to prevent groundwater contamination. The analysis should be conducted during the trial burn in addition to ongoing testing that may be required by local regulatory authorities. Releases of dust to air should also be controlled.

4.3.3 End-product control

168. Final products such as clinker or cement are subject to regular control procedures required by the usual quality specifications as laid down in applicable national or international quality standards.

169. As a principle, co-processing should not alter the quality of the cement being produced. This means that the product (clinker, cement, concrete) should not be abused as a sink for heavy metals; the product should not have any negative impact on the environment as, for example, demonstrated with leaching tests on concrete and/or mortar; and the quality of cement should allow end-of-life recovery.

170. Organic pollutants in the materials fed to the high temperature zone of the kiln system are completely destroyed, while the inorganic components are incorporated into the end product. 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 (European IPPC Bureau, 2009). 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).

171. As cement is blended with aggregates for the production of concrete or mortar, it is the behaviour of the metals in the building material (concrete or mortar) which is ultimately decisive for evaluating the environmentally relevant impacts of waste used in the clinker burning process (European IPPC Bureau, 2009). In this regard, the main results of leaching studies done to asses the environmental impacts of heavy metals embedded in concrete are as follows (GTZ/Holcim, 2006):

- The leached amounts of all trace elements from monolithic concrete (service life and recycling) are below or close the detection limits of the most sensitive analytical methods;
- 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;

- The leaching behaviour of concrete made with different cement types is similar;
- 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;
- 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);
- 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 end-of-life scenarios such as landfilling); and
- 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.

172. 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):

- Exposure of concrete structures in direct contact with groundwater (‘primary’ applications);
- Exposure of mortar or concrete to drinking water in distribution (concrete pipes) or storage systems (concrete tanks) (‘service life’ applications);
- Reuse of demolished and recycled concrete debris in new aggregates, road constructions, dam fillings etc. (‘secondary’ or ‘recycling’ applications); and
- Dumping of demolished concrete debris in landfills (‘end-of-life’ applications).

173. Careful selection and monitoring of the waste materials ensure that the use of wastes does not result in metal emissions of any environmentally harmful magnitude (European IPPC Bureau, 2009). However, in cases where the concentration of heavy metals exceeds the normal range found in cements made without alternative fuels and/or materials, leaching tests on mortar and/or concrete should be conducted (GTZ/Holcim, 2006).

174. For different, real-life concrete and mortar exposure scenarios, different leaching tests and assessment procedures need to be applied. Existing standardized test procedures have been developed mainly for waste regulations and drinking water standards, however there remains a need for harmonized and standardized compliance test procedures based on the exposure scenarios outlined above.

4.4. Monitoring

175. Emission monitoring is necessary to allow authorities to check compliance with the conditions in operating permits and regulations. For this purpose use of the following is good practice (European IPPC Bureau, 2003):

- Standard methods of measurement;
- Certified instruments;
- Certification of personnel; and
- Accredited laboratories.

4.4.1 Process monitoring

176. To control kiln processes, continuous measurements are recommended for the following parameters (European IPPC Bureau, 2009):

- Pressure
- Temperature
- O_2
- CO
- NOx
- SO_2

4.4.2 Emissions monitoring

177. To accurately quantify the emissions, continuous measurements are recommended for the following parameters:

- Exhaust gas flow rate
- Moisture
- Temperature
- O_2
- Dust (particulate matter)
- NOx
- SO_2
- CO
- Total organic compounds (TOC)

178. The operator should assure proper calibration, maintenance, and operation of the continuous emission monitoring systems (CEMS). A quality assurance program should be established to evaluate and monitor CEMS performance on a continual basis.

179. Periodical monitoring (minimum once per year) is appropriate for the following substances:

- Metals (Hg, Cd, Tl, As, Sb, Pb, Cr, Co, Cu, Mn, Ni, V) and their compounds
- HCl

- HF
- NH_3
- PCDDs/PCDFs

180. It is also possible to measure and monitor NH_3, Hg, HCl and HF continuously, and to sample PCCDs/PCDFs and PCBs continuously for analysis from 1 to 30 days (European IPPC Bureau, 2009).

181. Performance tests should be conducted to demonstrate compliance with the emission limits and performance specifications for continuous monitoring systems, when the kiln operates under normal operating conditions.

182. Measurements of the following may be required under special operating conditions (European IPPC Bureau, 2009):

- Benzene, toluene and xylene (BTX)
- Polycyclic aromatic hydrocarbons (PAHs), and
- Other organic pollutants (for example, chlorobenzenes, PCBs including coplanar congeners, chloronaphthalenes, etc.)

183. In case of disposal of wastes consisting of, containing or contaminated with persistent organic pollutants, the DRE should be determined (UNEP, 2007).

4.4.3 Environmental monitoring

184. Where there are justifiable concerns, an ambient air-monitoring programme may be required to monitor the environmental impact from the plant. This should assess environmental levels of key pollutants identified as a priority for 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 of significant interference from buildings or other structures.

4.4.4 Reporting requirements

185. Reporting of monitoring results involves summarising and presenting results, related information and compliance findings in an effective way.

186. Presentation of results for reporting purposes should indicate if exceedances or changes are significant when compared with the uncertainties in measurements and process parameters (European IPPC Bureau, 2003).

5. References

Achternbosch, M., Brautigam, K.R., Hartlieb, N., Kupsch, C., Richers, U., Stemmermann, P. and Gleis, M. 2003. Heavy metals in cement and concrete resulting from the co-incineration of wastes in cement kilns with regard to the legitimacy of waste utilisation. Forschungszentrum Karlsruhe. http://bibliothek.fzk.de/zb/berichte/FZKA6923.pdf

Baron, B., Reinaud, J., Genasci, M. and Philibert, C. 2007. Sectoral Approaches to Greenhouse Gas Mitigation: Exploring Issues for Heavy Industry. IEA Information Paper. International Energy Agency. http://www.iea.org/Textbase/publications/free_new_Desc.asp?PUBS_ID=2000

Battelle (Battelle Memorial Institute). 2002. Toward a Sustainable Cement Industry. Commissioned by the World Business Council for Sustainable Development. Available from http://www.wbcsd.org/web/publications/batelle-full.pdf [Accessed 24 May 2009]

British Geological Survey (BGS). 2005. Mineral Profile: Cement Raw Materials. British Geological Survey, Natural Environment Research Council http://www.bgs.ac.uk/MineralsUK/downloads/comm_profile_cement.pdf

CCME (Canadian Council of Ministers of the Environment). 1996. National Guidelines for the Use of Hazardous and Non-hazardous Wastes as Supplementary Fuels in Cement Kilns. Manitoba.

CEMBUREAU (The European Cement Association). 1999a. Environmental Benefits of Using Alternative Fuels in Cement Production: A Life-cycle Approach. Brussels. Available from http://www.cembureau.be/Publications-02.asp [Accessed 3 March 2009]

CEMBUREAU (The European Cement Association). 2009. Sustainable Cement Production: Co-processing of Alternative Fuels and Raw Materials in the European Cement Industry. Brussels. Available from http://www.cembureau.be/Publications-02.asp [Accessed 3 March 2009]

CPCB (Central Pollution Control Board). 2007. Comprehensive Industry Document on Vertical Shaft Kiln Based Mini Cement Plants. Ministry of Environment & Forests, Government of India. Available from http://www.cpcb.nic.in/oldwebsite/New%20Item/mini_cement_plant.html [Accessed 5 March 2009]

Da Hai, Y., Karstensen, K.H., Qi, W., Qifei, H. and Mulin, C. 2009. Co-processing of Industrial and Hazardous Wastes in Cement Kilns in China - A Review of Current Status and Future Needs. *Accepted for publication in Environmental Engineering Science*.

Degré, J.P. 2009. *Co-processing in Cement Kilns: The Holcim Approach and Experience.* Presented at "Taller Co-procesamiento de Residuos Peligrosos en Hornos Cementeros", Santiago. 9 June.

Department for Environmental Affairs and Tourism, Republic of South Africa. 2009. National Policy on Thermal Treatment of General and Hazardous Waste. Government Gazette (Staatskoerant), 24 Julie 2009.

EA (Environment Agency of England and Wales). 1999a. International Use of Substitute Liquid Fuels (SLF) Used for Burning in Cement Kilns. Research and Development Technical Report P282. Bristol: Environment Agency.

EA (Environment Agency of England and Wales). 1999b. Substitute Liquid Fuels (SLF) Used in Cement Kilns – Life Cycle Analysis. Research and Development Technical Report P274. Bristol: Environment Agency.

EA (Environment Agency of England and Wales). 2005. Measuring Environmental Performance: Sector Report for the Cement Industry. Version 1. Bristol: Environment Agency.

Environment Council. 2007. Designing Engagement for the Waste Sector. London: The Environment Council. Available from http://www.the-environment-council.org.uk/index.php?option=com_docman&task=cat_view&gid=78&Itemid=64 [Accessed on 2 November 2009]

European IPPC Bureau. 2003. Integrated Pollution Prevention and Control, Reference Document on the General Principles of Monitoring (July 2003). European Commission, Joint Research Centre, Institute for Prospective Technological Studies. Seville. Available from ftp://ftp.jrc.es/pub/eippcb/doc/mon_bref_0703.pdf [Accessed 19 August 2009]

European IPPC Bureau. 2006. Integrated Pollution Prevention and Control, Draft Reference Document on Best Available Techniques for the Waste Treatment Industries (August 2006). European Commission, Joint Research Centre, Institute for Prospective Technological Studies. Seville.

European IPPC Bureau. 2009. Integrated Pollution Prevention and Control, Draft Reference Document on Best Available Techniques in the Cement, Lime and Magnesium Oxide Manufacturing Industries (May 2009). European Commission, Joint Research Centre, Institute for Prospective Technological Studies. Seville. Available from ftp://ftp.jrc.es/pub/eippcb/doc/clm_bf_0509_public.pdf [Accessed 19 August 2009]

Greer, W.L. 2003. Interactions Among Gaseous Pollutants from Cement Manufacture and Their Control Technologies. R&D Serial No. 2728. Portland Cement Association, Skokie, Illinois.

GTZ/Holcim. 2006. Guidelines on Co-Processing Waste Materials in Cement Production. The GTZ- Holcim Public Private Partnership.

Höhne, N. and Ellermann, C. 2008. A Sectoral Approach and Technology Transfer for the Cement Sector. Federal Office for the Environment (FOEN), Switzerland. Available from http://www.bafu.admin.ch/klima/index.html?lang=en&download=NHzLpZeg7t,lnp6I0NTU042l2Z6ln1ad1IZn4Z2qZpnO2Yuq2Z6gpJCFeYR6fGym162epYbg2c_JjKbNoKSn6A--.pdf [Accessed 5 March 2009]

Hund, G., Engel-Cox, J., Fowler, K., Peterson, T., Selby, S. and Haddon, M. 2002. Communication and Stakeholder Involvement: Guidebook for Cement Facilities. Battelle Memorial Institute and Environmental Resources Management (ERM) Ltd. Commissioned by the World Business Council for Sustainable Development. Available from http://www.wbcsdcement.org/pdf/battelle/stakeholder_guide.pdf [Accessed 24 May 2009]

IEA (International Energy Agency). 2007. Tracking Industrial Energy Efficiency and CO2 Emissions, In Support of the G8 Plan of Action. International Energy Agency (IEA), Organisation for Economic Co-operation and Development (OECD).

IPCC, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., Davidson, D., de Coninck, H., Loos, M. and Meyer, L. (eds.)]. Cambridge University Press. Available from http://www.ipcc.ch/publications_and_data/publications_and_data_reports_carbon_dioxide.htm [Accessed 20 August 2009]

Karstensen, K. H. 2008b. Formation, release and control of dioxins in cement kilns - A review. Chemosphere, 70 (2008) 543–560.

Karstensen, K. H. 2009a. Guidelines for co-processing. Proceedings of "China International Conference on the Utilization of Secondary Materials and Fuel in Building Materials Industry". Institute of Technical Information for Building Materials Industry of China, No.1, Guanzhuang Dongli, Chaoyang District, Beijing, China. Beijing International Exhibition Center. 29 June 2009.

Karstensen, K. H. 2009b. Requirements for Co-Processing of AFR and Treatment of Organic Hazardous Wastes in Cement Kilns. Proceedings of "China International Conference on the Utilization of Secondary Materials and Fuel in Building Materials Industry". Institute of Technical Information for Building Materials Industry of China, No.1, Guanzhuang Dongli, Chaoyang District, Beijing, China. Beijing International Exhibition Center. 29 June 2009.

Karstensen, K.H. 2009c. Performance Verification and Test Burns in Cement Kilns: A Compilation. Oslo: Foundation for Scientific and Industrial Research (SINTEF).

Karstensen, K.H. 2006a. Cement Production in Vertical Shaft Kilns in China: Status and Opportunities for Improvement. Report to the United Nations Industrial Development Organization. Available from http://coprocem.ecs.ch/documents/3cementproductioniinverticalshaftkilnschina.pdf [Accessed 5 January 2009]

Karstensen, K.H. 2006b. Formation and Release of POPs in the Cement Industry. Second edition. World Business Council for Sustainable Development/SINTEF. Available from http://www.wbcsd.org/plugins/DocSearch/details.asp?type=DocDet&ObjectId=MTgyNzM [Accessed 10 November 2008]

Karstensen, K.H. 2007a. A Literature Review on Co-processing of Alternative Fuels and Raw Materials and Hazardous Wastes in Cement Kilns. Department for Environmental Affairs and Tourism, Republic of South Africa. Available from http://www.environment.gov.za/hotissues/2008/cementproduction/cement.html [Accessed 2 January 2009]

Karstensen, K.H. 2007b. National policy on High Temperature Thermal Waste Treatment and Cement Kiln Alternative Fuel Use: Cement Production Technology. Department Environmental Affairs and Tourism of the Republic of South Africa. Available from http://www.deat.gov.za//PolLeg/GenPolicy/2008Sep25/cement.html [Accessed 2 January 2009]

Karstensen, K.H. 2008a. National policy on High Temperature Thermal Waste Treatment and Cement Kiln Alternative Fuel Use: Guidelines for Co-processing of Alternative Fuels and Raw Materials and Treatment of Organic Hazardous Wastes in Cement Kilns. Department Environmental Affairs and Tourism of the Republic of South Africa. Available from http://www.deat.gov.za//PolLeg/GenPolicy/2008Sep25/cement.html [Accessed 2 January 2009]

Karstensen, K.H., Nguyen, K.K., Le B.T., Pham, H.V., Nguyen, D.T., Doan, T.T., Nguyen, H.H., Tao, M.Q., Luong, D.H. and Doan, H.T. 2006. Environmentally sound destruction of obsolete pesticides in developing countries using cement kilns. Environmental Science & Policy, 9 (2006), 577-586

Koppejan, J. and Zeevalkink, J.A. 2002. The calorific value as a criterion for waste recovery in the cement industry. TNO-Report R 2002/325. TNO Netherlands Organisation for Applied Scientific Research. Apeldoorn: TNO. Available from http://www.coprocem.com/documents/energy-rapport-2002-325lhv-cement.pdf [Accessed 2 July 2009]

Loréa, C. 2007. The Co-processing of Waste in the Cement Industry. Global Fuels Magazine. June, p.12-15. Available from http://www.propubs.com/GF/Articles/eGF_Jun07_Cembureau.pdf [Accessed 1 April 2009]

Mantus, E.K. 1992. All fired up: Burning Hazardous Waste in Cement Kilns. Washington: Environmental Toxicology International.

Murray, A. and Price, L. 2008. Use of Alternative Fuels in Cement Manufacture: Analysis of Fuel Characteristics and Feasibility for Use in the Chinese Cement Sector. China Energy Group, Ernest Orlando Lawrence Berkeley National Laboratory, U.S. Department of Energy. http://china.lbl.gov/node/159

Mutz, D., Andres, C., Hengevoss, D. and Morf, L. 2007. Co-Processing Waste Material in Energy-Intensive Industries (EII): A global study with focus on Europe. University of Applied Sciences Northwestern Switzerland, GEO Partner AG Resource Management.

OECD (Organisation for Economic Co-operation and Development). 2000. Strategic Waste Prevention, OECD Reference Manual. ENV/EPOC/PPC(2000)5/FINAL.

SBC (Secretariat of the Basel Convention). 2007. Updated general technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (POPs). Available from http://www.basel.int/pub/techguid/tg-POPs.pdf [Accessed on 1 April 2009]

Szabó, L., Hidalgo, I., Císcar, J.C., Soria, A. and Russ P. 2003. Energy consumption and CO2 emissions from the world cement industry. Report EUR 20769 EN. Institute for Prospective Technological Studies, Joint Research Center, European Commission. http://ftp.jrc.es/EURdoc/eur20769en.pdf

Taylor, H.F.W. 1997. Cement chemistry. Second edition. Thomas Telford, London.

Twigger, L., Ritchie, A., Hudson, B., Laban, K. And Davies, C. 2001. Solid Waste Derived Fuels for Use in Cement & Lime Kilns - An International Perspective. Research and Development Technical Report P4-087/TR/1. Bristol: Environment Agency.

U.S. EPA (U.S. Environmental Protection Agency). 1993. Report to Congress on Cement Kiln Dust. Available from: http://epa.gov/wastes/nonhaz/industrial/special/ckd/cement2.htm [Accessed 3 March 2009]

U.S. EPA (U.S. Environmental Protection Agency). 1996. RCRA Public Participation Manual, 1996 Edition. Office of Solid Waste. Washington: U.S. Environmental Protection Agency. Available from http://www.epa.gov/waste/hazard/tsd/permit/pubpart/manual.htm [Accessed on 2 November 2009]

U.S. EPA (U.S. Environmental Protection Agency). 1998. National Emission Standards for Hazardous Air Pollutants; Proposed Standards for Hazardous Air Pollutants Emissions for the Portland Cement Manufacturing Industry; Proposed Rule. 40 CFR part 63, March 24, 1998, 63 FR 14181. Available from http://www.epa.gov/ttn/atw/pcem/pcempg.html [Accessed on 11 March 2010]

U.S. EPA (U.S. Environmental Protection Agency). 2004. Draft Technical Support Document for HWC MACT Standards. Volume I: Description of Source Categories. Office of Solid Waste and Emergency Response. Washington: U.S. Environmental Protection Agency.

U.S. EPA (U.S. Environmental Protection Agency). 2007. Cement. In: Energy Trends in Selected Manufacturing Sectors: Opportunities and Challenges for Environmentally Preferable Energy Outcomes. Available from: http://www.epa.gov/ispd/energy/index.html [Accessed 2 March 2009]

U.S. Geological Survey. 2009. Cement. In: Mineral Commodity Summaries 2009. Washington: U.S. Geological Survey. Available from: http://minerals.usgs.gov/minerals/pubs/mcs/ [Accessed 2 March 2009]

UNEP (United Nations Environment Programme). 2007. Guidelines on Best Available Techniques and Provisional Guidance on Best Environmental Practices Relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants: Cement Kilns Firing Hazardous Waste. Expert Group on Best Available Techniques and Best Environmental Practices. Geneva: UNEP.

UNSD (United Nations Statistics Division). 2008. United Nations Commodity Trade Statistics Database (UN Comtrade). http://comtrade.un.org/db/

Van der Sloot, H.A., van Zomeren, A., Stenger, R., Schneider, M., Spanka, G., Stoltenberg-Hansson, E. and Dath, P. 2008. Environmental CRIteria for CEMent Based Products, ECRICEM. Executive Summary. Energy Research Centre of the Netherlands (ECN). ECN Report N° ECN-E--08-011. Available from http://www.ecn.nl/docs/library/report/2008/e08011.pdf [Accessed 10 March 2009]

Van Oss, H.G. 2005. Background Facts and Issues Concerning Cement and Cement Data. Open-File Report 2005-1152. U.S. Department of the Interior, U.S. Geological Survey.

Van Oss, H.G. and Padovani, A.C. 2003. Cement manufacture and the environment. Part II: Environmental Challenges and Opportunities. Journal of Industrial Ecology, 7 (1), 93-126.

Watson, C., Newman, J., Upton, S. and Hackmann, P. 2005. Round Table on Sustainable Development: Can Transnational Sectoral Agreements Help Reduce Greenhouse Gas Emissions? SG/SD/RT(2005)1. Organisation for Economic Co-operation and Development. http://www.oecd.org/dataoecd/35/53/39357524.pdf

WBCSD (World Business Council for Sustainable Development). 2005. Guidelines for the Selection and Use of Fuels and Raw Materials in the Cement Manufacturing Process. Cement Sustainability Initiative (CSI). Geneva: WBCSD. Available from http://www.wbcsd.org/includes/getTarget.asp?type=d&id=MTc4NjA [Accessed 9 October 2008]

Zeevalkink, J.A. 1997. The Materials and Energy Potential Method for the Quantitative Distinction Between Waste Valorization and Elimination in the Cement Industry. TNO-Report TNO-MEP - R 96/502. TNO Institute of Environmental Sciences, Energy Research and Process Innovation. Apeldoorn: TNO.

Annex 1. Clinker Production Process

1. Cement production involves the heating, calcining and sintering of a carefully proportioned mixture of calcareous and argillaceous materials, usually limestone and clay, to produce cement clinker, which is then cooled and ground with additives such as gypsum (a setting retardant) to make cement. This process typically requires approximately 2,9 to 6,7 GJ of energy depending on the kiln technology employed (IEA, 2007) and 1,5 to 1,7 tonnes of raw materials per tonne of clinker produced (Szabó et al, 2003); the portion of raw material that does not become clinker is either lost on ignition or becomes CKD (U.S. EPA, 1993). 'Wet' processes also use water to make the raw slurry that feeds the kilns; about 600 kg of water is used in the manufacture of one tonne of cement, some of which is returned to the environment (EA, 2005).

187. Manufacturers use clinker and specific constituents in various proportions to produce cements that meet different physical and chemical requirements for specific applications. By far the most common hydraulic cements in use today are either Portland cements or 'blended' cements (van Oss and Padovani, 2003). The standard specifications with which Portland cements must comply are similar (albeit not identical) in all countries and various names are used to define the material. Blended cements, also called composite cements, are mixtures of Portland cement with one or more pozzolanic additives or extenders (sometimes collectively termed 'supplementary cementitious materials'), such as pozzolana (volcanic ashes), certain types of fly ash (from coal-fired powerplants), granulated blast furnace slag, silica fume, or limestone. These materials commonly make up about 5% to 30% by weight of the total blend, but can be higher (van Oss, 2005). The designations for blended cements differ worldwide.

188. Although a variety of cement types are produced worldwide, cement production follows essentially the same process, as described below.

Conventional Raw Materials and Fuel

189. The raw materials for cement must yield the oxides required for clinker in the approximate proportions noted in Table 1, with the major requirement being calcium oxide (CaO). In practical terms this means that naturally occurring calcareous deposits, such as limestone, marl or chalk, which consist essentially of calcium carbonate ($CaCO_3$), are required. Clay or shale typically provides the remaining components. To correct for minor deficiencies in one or more oxides in the primary raw materials, 'corrective' constituents[7] such as iron ore, bauxite or sand, may be added to adapt the chemical composition of the raw mix to the requirements of the process and product specifications (Taylor, 1997; Karstensen, 2007b). Generally, most, but not all, of the raw materials are mined adjacent to or within a few miles of the cement plant.

Table 1. Chemical composition of ordinary Portland cement clinker and conventional raw materials

Constituent	Clinker	Limestone, lime marl, chalk	Clay	Sand	Iron ore	Bauxite
SiO_2	19,71-24,25%	0,5-50%	33-78%	80-99%	4-11%	2,9%
Al_2O_3	3,76-6,78%	0,1-20%	7-30%	0,5-7%		

---

[7] Sometimes called accessory or 'sweetener' materials (van Oss, 2005).

Constituent	Clinker	Limestone, lime marl, chalk	Clay	Sand	Iron ore	Bauxite
TiO_2	0,21-0,52%	0,0-0,7%	0,2-1,8%	0,0-0,5%		
$Al_2O_3 + TiO_2$			7-30%	0,5-2%	0,2-3%	57,5%
Fe_2O_3	1,29-4,64%	0,2-5,9%	4,0-15%	0,0-4%		
Mn_2O_3	0,03-0,68%	0,02-0,15%	0,09%	0,051%		
$Fe_2O_3 + Mn_2O_3$		0,1-10%	2-15%	0,5-2%	19-95%	22,8%
CaO	63,76-70,14%	20-55%	0,2-25%	0,1-3%	0,1-34%	2,4%
MgO	0,00-4,51%	0,2-6%	0,3-5%	0,3-0,5%	≤ 1,5%	0,04%
K_2O	0,31-1,76%	0-3,5%	0,4-5%	0,2-3%	Traces	0,04%
Na_2O	0,03-0,335	0,0-1,5%	0,1-1,5%	0,0-1%	Traces	0,02%
Cl		0,0-0,6%	0,0-1%	Traces		
P_2O_5	0,02-0,27%	0,0-0,8%	0,0-1,0%	0,0-0,1%		
Loss on ignition ($CO_2 + H_2O$)	0,09-1,56%	2-44%	1-20%	≤ 5	0,1-30%	13,5%

Sources: European Commission (2009) and CEMBUREAU (1999)

190. Natural forms of $CaCO_3$ consist of coarser or finer crystals of calcite. Limestone is microcrystalline $CaCO_3$ with clay as the main impurity. Chalk is a very fine grained, porous marine limestone composed almost entirely of microscopic fossils. The main constituents of shale and clay are clay minerals, finely divided quartz and, sometimes, iron oxides. Traditionally, wet materials (chalk and clay) have been used in 'wet' or 'semi-wet' kiln processes, and dry materials (limestone) have been used in the 'dry' or 'semi-dry' processes (EA, 2005).

191. Around 80-90% of raw material for the kiln feed is limestone; clayey raw material accounts for between 10-15%, although the precise amounts will vary (BGS, 2005). In addition to the chemical composition of the desired product, the proportion of each type of raw material used in a given cement kiln will depend on the composition of the specific materials available to the operator, which is tested on a regular basis.

192. The proportioning process takes into account the ratios of calcium, silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) needed to produce good quality clinker, as well as the 'burnability' of the raw mix (i.e., the requirements in terms of time, temperature, and fuel to process the material) (U.S. EPA, 1993). In addition, kiln operators pay close attention to the presence of 'impurities' in the mixture, including magnesia, sulphur, chlorides, and oxides of potassium and sodium (referred to as 'alkalies'). Magnesia (MgO) can be desirable to some extent because it acts as a flux at sintering temperatures, facilitating the burning process, however MgO levels are carefully monitored because they can lead to the production of clinker that is unsound if not cooled rapidly[8]. Alkalies can react in the cool end of the kiln with sulphur dioxide, chlorides, and carbon dioxide contained in the kiln gas and can lead to operational problems (U.S. EPA, 1993).

193. The raw materials used in the cement production process naturally contain metals and halogens. Thus, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, thallium, vanadium, zinc, bromine, chlorine, fluorine, and iodine are typically present in the raw materials. The amounts of these components depend on the geological formations from which the raw materials are mined. In addition to the metals and halogens present, the raw

---

[8] Such clinker used to make concrete can cause destructive expansion of hardened concrete through slow reaction with water.

materials can contain organic compounds (Mantus, 1992). Average values and range of concentrations of these constituents are presented in Table 2.

194. Cement production also has high energy requirements, which typically account for 30-40% of the production costs (excluding capital costs). Most cement kilns today use coal and petroleum coke as primary fuels, and to a lesser extent natural gas and fuel oil. As well as providing energy, some of these fuels, especially coal or lignite, which produce significant quantities of ash similar in composition to the argillaceous component.

195. Many plants routinely burn more than one fuel. For example, when firing up a cold kiln, natural gas or fuel oil is commonly used for the slow, warm-up phase necessary to prevent thermal overstressing of the kiln's refractory brick lining. Once the kiln is sufficiently hot, it will be switched over to coal and/or coke (generally petroleum coke) for production operations. (van Oss, 2005)

196. Coal can contain significant quantities of sulphur, trace metals, and halogens, and their concentrations are dependent on the area in which the coal was mined (see Table 3). Sulphur (in the form of SO_3) will vaporize in the kiln to form sulphur dioxide (SO_2), and condense in the form of sulphates. Within the kiln, these sulphates combine with calcium and potassium, causing operational problems in the cool end of the kiln. Halogens are of concern because chlorides can cause operational problems similar to those caused by sulphur. Chlorine concentrations in coal can range from 100 to 2800 parts per million. (U.S. EPA, 1993)

197. Both heat and electricity consumption vary significantly with kiln technology (see Table 4) and, for the same general technology, plants operating multiple kilns tend to have higher energy requirement per tonne of overall output capacity than do plants with the same overall capacity but that operate a single kiln. Wet kilns consume more fuel on a unit basis than do dry kilns because of the need to evaporate the water in the slurry feed and the much larger size of the wet kilns. (van Oss, 2005)

Table 2. Trace element concentrations (in parts per million) in conventional raw materials (Min = minimum value; Max = maximum value; AV = average value; n.a. = no data available)

Constituent	Limestone		Marl		Clay		Sand		Iron ore		Gypsum/anhydrite	
	Min-Max	(AV)	Min-Max	(AV)	Min-Max	(AV)	Min-Max	(AV)	Min-Max	(AV)	Min-Max	(AV)
As	0,1-15	(3)	0,2-12	(6)	2-100	(14)	0,4-42	(11)	2-1200	(37)	0,2-3,5	(1,5)
Be	0,01-12	(0,3)	n.a.-1	(0,5)	1-7	(3)	0,6-1,5	(1,0)	0,8-2	(1)	0,02-0,9	(0,2)
Cd	0,02-2	(0,2)	0,02-0,5	(0,3)	0,01-1	(0,2)	0,01-1	(0,2)	0,02-15	(6)	0,03-2,3	(0,15)
Co	0,1-7	(3)	n.a.-28	(5)	6-25	(20)	0,3-37	(11)	109-183	(144)	0,02-3,9	(1)
Cr	0,5-184	(14)	1,2-71	(28)	15-260	(85)	1-220	(19)	8-1400	(495)	1-27,3	(8,8)
Cu	5-57	(11)	4,9-35	(12)	10-285	(43)	1,2-85	(10)		(1520)	0,3-12,8	(7)
Hg	0,005-0,1	(0,04)	0,005-0,1	(0,03)	0,01-0,5	(0,2)	0,01-1	(0,02)	n.a.-1	(0,5)	0,00625-1,3	(0,1)
Mn	250-3300	(500)	n.a.-3300	(360)	n.a.-2500	(600)	46-2040	(194)	900-1200	(1090)	n.a.	
Ni	1,4-131	(18)	1,5-57	(16)	7-236	(63)	1-73	(13)	5-815	(331)	0,3-14,5	(5,5)
Pb	0,27-151	(18)	0,3-57	(12)	1-219	(25)	0,7-70	(10)	4-8700	(350)	0,2-20,5	(7)
Sb	0,2-27	(1)	n.a.-27	(4)	0,5-13	(2)	0,3-12	(7)		(26)	0,1-5	(1)
Se	0,4-30	(0,6)	n.a.	(1)	n.a.-2,5	(0,5)	n.a.	(1)		(8)	0,6-17	(0,8)
Sn	0,9-24	(4)	n.a.-24	(3)	1,6-30	(5)	1,8-40	(3)	n.a.-500	(25)	n.a.	
Te	n.a.	(0,7)	n.a.	(1)	n.a.	(0,5)	n.a.	(0,5)	n.a.-13	(10)	n.a.	
Tl	0,05-3	(0,3)	0,05-0,68	(0,6)	0,1-1,6	(0,5)	0,05-1	(0,2)	0,1-400	(2)	0,1-1,0	(0,3)
V	5-80	(26)	n.a.-49	(20)	30-300	(130)	2-240	(50)	10-690	(256)	1-27,8	(13,5)
Zn	0,1-229	(30)	22-79	(48)	2-304	(78)	4,2-112	(25)	24-9400	(3288)	1-59	(19)
Br a/	n.a.	(5,9)	n.a.		1-58		n.a.		n.a.		n.a.	
Cl a/	50-240		n.a.		15-450		n.a.		n.a.		n.a.	
F a/	100-940		n.a.		300-990		n.a.		n.a.		n.a.	
I a/	0,25-0,75		n.a.		0,2-2,2		n.a.		n.a.		n.a.	

a/ Mantus (1992)

Source: Achternbosch et al. (2003), unless otherwise noted.

Table 3. Trace element concentrations (in parts per million) in primary fuels (Min = minimum value; Max = maximum value; n.a. = no data available)

Constituent	Anthracite Min-Max	Bituminous coal Min-Max	Lignite Min-Max	Petroleum coke Min-Max
As	1-200	n.a.	0,1-12	0,2-0,8
Be	0-8	n.a.	0,04-0,6	0,02-0,03
Cd	0,01-10	n.a.	0,06-2,4	0,04-4
Co	0,5-43	n.a.	0,5-4,2	n.a.
Cr	1-260	n.a.	0,9-20	0,9-104
Cu	0,30-60	n.a.	0,4-15	n.a.
Hg	0,01-3	n.a.	0,01-0,7	0,01-0,09
Mn	5-356	n.a.	50-160	n.a.
Ni	1-110	n.a.	0,6-29	24-355
Pb	5-270	n.a.	0,7-34	1-102
Sb	0,05-5	n.a.	0,04-2,5	n.a.
Se	0-6	n.a.	0,4-25	n.a.
Sn	1,3-7,8	n.a.	0,5-15	n.a.
Te	0,2-5,0	n.a.	0,1-10	n.a.
Tl	0,1-5	n.a.	0,05-0,4	0,04-3,1
V	10-250	n.a.	0,1-84	45-1435
Zn	4,5-405	n.a.	1-70	16-220
Br a/	n.a.	7-11	n.a.	n.a.
Cl a/	n.a.	100-2800	n.a.	n.a.
F a/	n.a.	50-370	n.a.	n.a.
I a/	n.a.	0,8-11,2	n.a.	n.a.

a/ Mantus (1992)

Source: Achternbosch et al. (2003), unless otherwise noted.

Table 4. Energy requirements for clinker manufacture

Process	Fuel consumption, GJ/tonne
Vertical shaft kiln	3,7-6,6
Wet process	5,9-6,7
Long dry process	4,6
1 stage cyclone preheater	4,2
2 stage cyclone preheater	3,8
4 stage cyclone preheater	3,3
4 stage preheater + precalciner	3,1
5 stage preheater + precalciner	3,0-3,1
6 stage preheater + precalciner	2,9

Source: IEA (2007) and Szabó (2003)

Manufacturing Process

198. Portland cement manufacture begins with the manufacture of clinker followed by the fine grinding of the clinker with gypsum and other additives to make the finished cement product.

Grinding can occur on site or at offsite grinding plants (cement mills). Clinker manufacture itself involves first the quarrying, crushing, and proportioning of raw materials to produce either a raw meal for the dry (and semi-dry) process or a slurry for the wet (and semi-wet) process. Once the material is prepared, it is fed into a kiln where the heating of the raw mix as it moves through the kiln drives a number of chemical and physical processes which are necessary to form the clinker.

199. In the kiln, the raw meal (or slurry in the wet process) is subjected to a thermal treatment process consisting of the consecutive steps of 'drying/preheating', 'calcining', and 'sintering' (also known as 'burning' or 'clinkering'); the various reactions zones are depicted in Figure 1. In the first drying and preheating zone, occurring in a temperature range of <100 to 750°C, residual (free) water is evaporated from the raw meal feed, and clay materials begin to decompose and are dehydrated (removing bound water). Next, in the calcining zone (with materials temperatures ranging from 750 to 1000°C) the material is 'calcined'; that is calcium carbonate ($CaCO_3$) in the limestone is dissociated producing calcium oxide (CaO, lime) and liberating gaseous carbon dioxide (CO_2). Finally, in the burning zone, calcium oxide reacts with silicates, iron, and aluminium to form dicalcium silicate, tricalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite (denoted in shorthand: C_2S, C_3S, C_3A, and C_4AF respectively). In addition, clinker nodules, typically 3 to 20 mm in diameter, are formed in a semi-solid state in the burning zone, and solidify completely on cooling, which begins in a short cooling zone within the kiln, and continues in a cooler, outside of the cement kiln.

200. In the clinker burning process, it is essential to maintain kiln charge temperatures in the sintering zone between 1400 and 1500°C to convert the raw meal to clinker. To reach these temperatures, flame temperatures of about 2000°C are necessary. Also, for reasons of clinker quality, excess air is required in the sintering zone to maintain oxidizing conditions. Otherwise, if insufficient oxygen is present, tetracalcium alumino ferrite does not form; instead Fe_2O_3 is reduced to FeO. This leads to a clinker product that produces a quick setting cement with decreased final strength. Additionally, the presence of unburned carbon in the burning region produces a clinker with an undesirable brown colour. (U.S. EPA, 2004)

201. The composition of the clinker, as well as the names and formulas of the clinker components are listed in Table 5. To complete the production of Portland cement, the cooled clinker is ground with a small amount of gypsum or anhydrite. Figure 2 provides a process flow diagram of the general cement manufacturing process.

Table 5. Typical mineralogical composition of ordinary Portland cement clinker

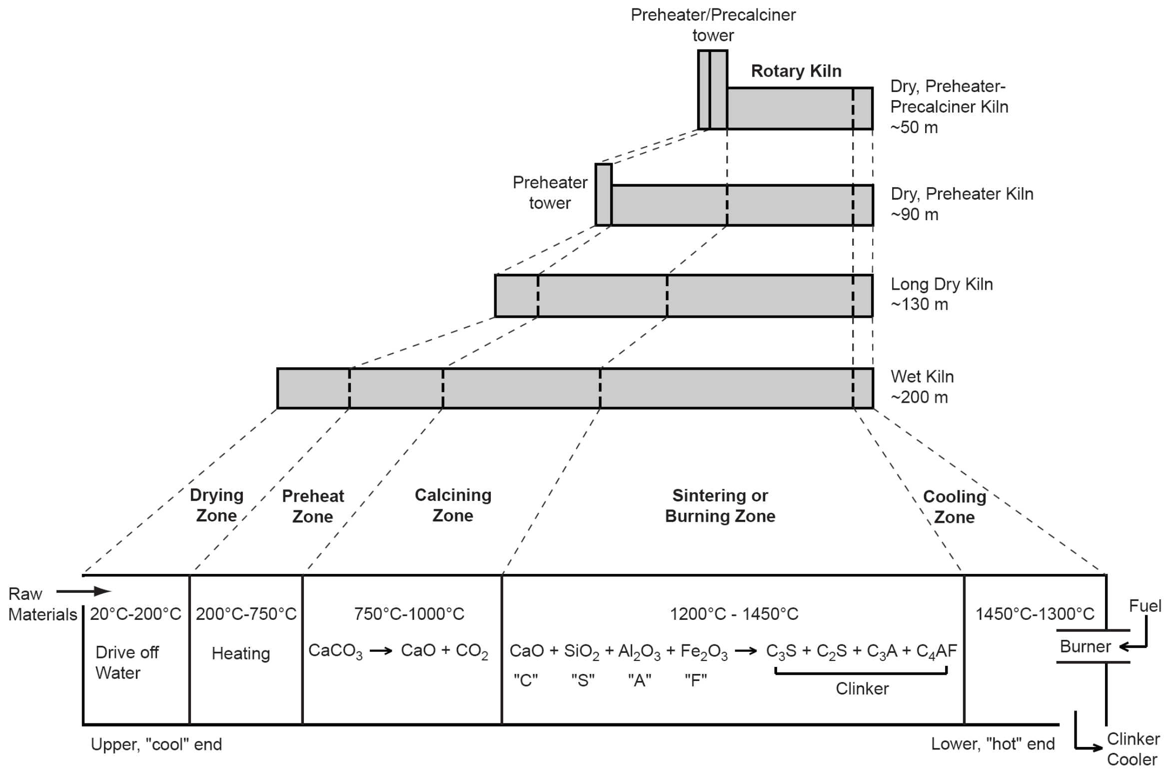
Chemical name (common name)	Chemical formula	Common notation a/	Concentration range
Tricalcium silicate ('alite')	Ca_3SiO_5	C_3S	50-70%
Dicalcium silicate ('belite')	Ca_2SiO_4	C_2S	15-30%

Tricalcium aluminate (‘aluminate’)	$Ca_3Al_2O_6$	C_3A	5-10%
Tetracalcium aluminoferrite (‘ferrite’)	$Ca_4Al_2Fe_2O_{10}$	C_4AF	5-15%

a/ Abbreviations: C=CaO; S=SiO_2; A=Al_2O_3; F=Fe_2O_3

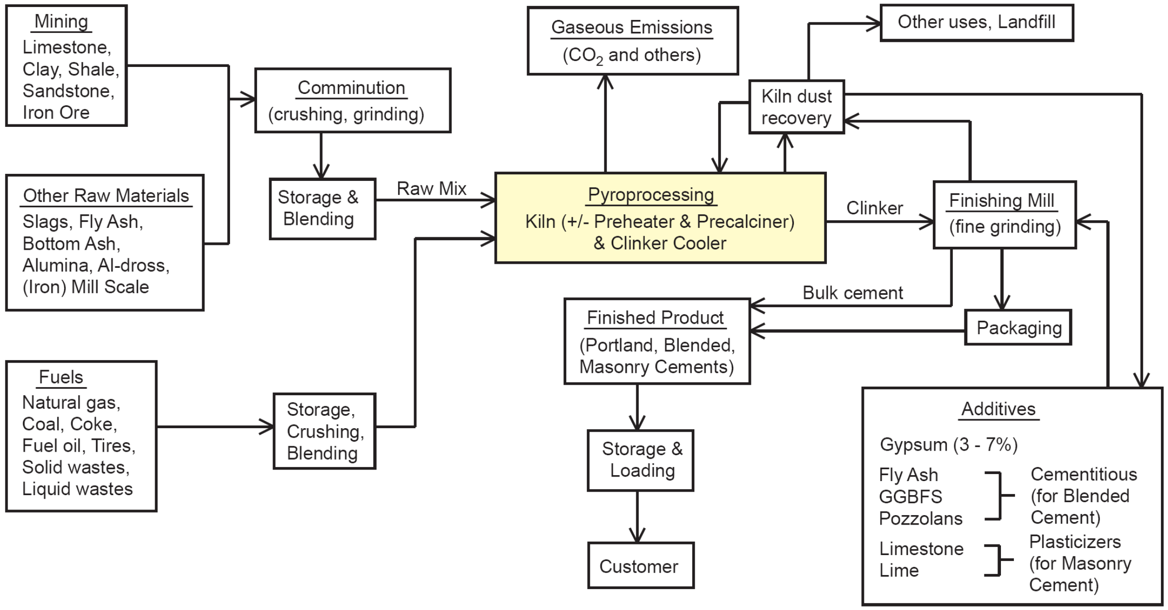
Source: Taylor (1997)

Figure 1. Diagram of ‘reaction’ zones for different kiln technologies



Source: van Oss (2005)

Figure 2. General cement manufacturing process



Source: van Oss (2005)

202. Clinker can be made either in energy-intensive and small-scale vertical kilns or in more efficient, larger scale rotary kilns. 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. For the manufacture of cement using rotary kilns heating of the raw meal to produce cement clinker can take place in one of four different types of arrangements: the 'dry', 'semi-dry', 'semi-wet', or 'wet' processes (European Commission, 2001; UNEP, 2006):

- Dry process: Dry raw meal is fed to a cyclone preheater or precalciner kiln or, in some cases, to a long dry kiln with internal chain preheater.
- Semi-dry process: Dry raw meal is pelletised with water and fed to a travelling grate preheater prior to the rotary kiln or in some cases, to a long kiln equipped with internal cross preheaters.
- Semi-wet process: Raw slurry is first dewatered in filter presses. The resulting filter cake is either extruded into pellets and fed to a travelling grate preheater or fed directly to a filter cake drier for (dry) raw meal production prior to a preheater/precalciner kiln.
- Wet process: The raw slurry is fed either directly to a long rotary kiln equipped with an internal drying/preheating system (conventional wet process) or to slurry drier prior to a preheater/precalciner kiln (modern wet process).

203. In China approximately 60 percent of the cement was produced in 2005 in VSKs, an amount that is expected to drop to 50 percent by 2015 (Karstensen, 2006a). In Europe, about 78 percent of the cement production is from dry process kilns, a further 16 percent of production is accounted for

by semi-dry and semi-wet process kilns, with the remainder of European production, about 6 percent, coming from wet process kilns (European Commission, 2001). In the United States, no new wet kilns have been built since 1975, and approximately 80 percent of U.S. cement production capacity now relies on the dry process technology (U.S. Environmental Protection Agency, 2007). The wet process remains dominant in the former Soviet Union and Australia/New Zealand and is still significant in Canada, India, Latin America and Africa (Watson et al., 2005). Table 6 provides the share mix of kiln technologies in each region or country in 2002.

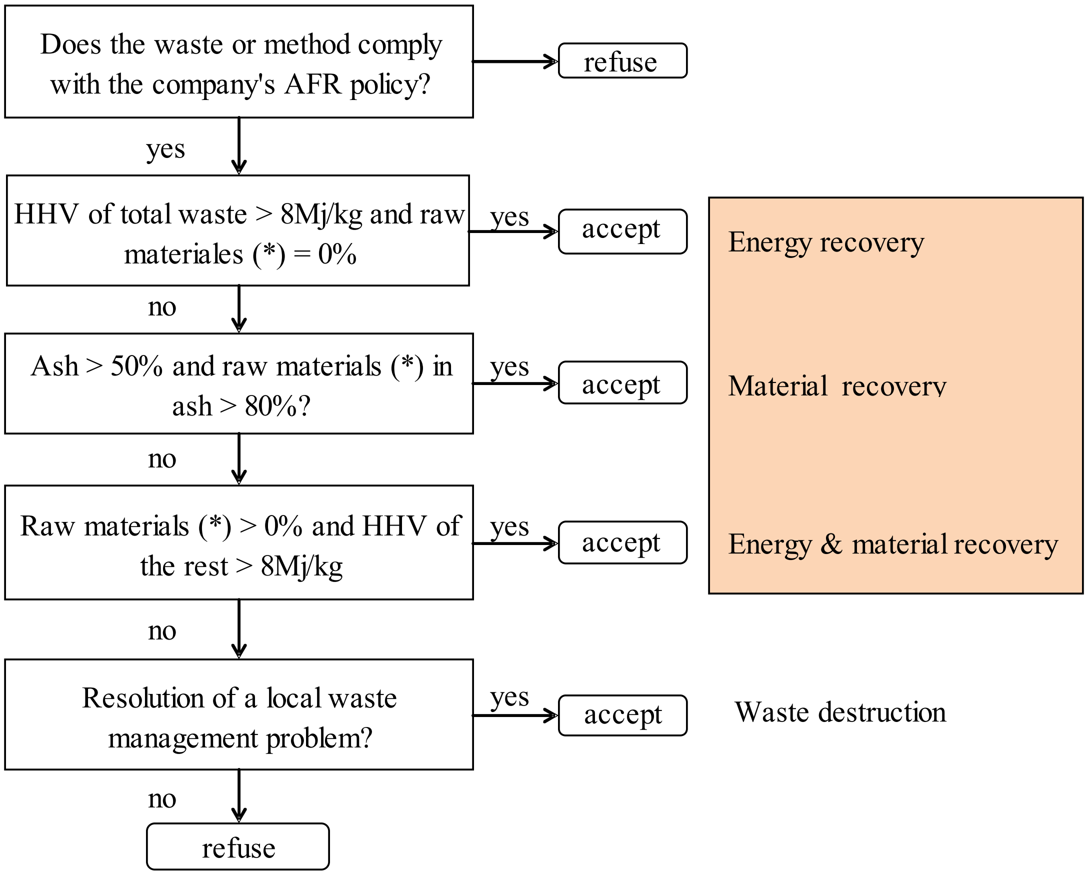
204. Although VSKs are improvements over the old, chimney-type kilns in that some VSKs allow for continuous processing, they are considered to be less energy efficient than the rotary kilns, and VSK clinker (and hence cement) is generally considered to be of lower quality (van Oss, 2005). Furthermore, 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. Compared with preheater/precalciner kilns, VSKs seems to consume from 14 % to 105 % more coal per tonne of clinker; fuel substitution is however not feasible for vertical shaft kilns (Karstensen, 2006a). The raw materials used for cement production in VSKs are exactly the same as in any other production process; corrective materials may also be required to adjust the chemical composition of the raw mix.

Table 6. Share of different kiln types in 2002

Regions, Countries		Kiln Type (% Production)			
		Dry	Semi-Dry	Wet	Vertical
North America	United States	65	2	33	0
	Canada	71	6	23	0
Western Europe		58	23	13	6
Asia	Japan	100	0	0	0
	Australia and New Zealand	24	3	72	0
	China	5	0	2	93
	South East Asia	80	9	10	1
	Republic of Korea	93	0	7	0
	India	50	9	25	16
Eastern Europe	Former Soviet Union	12	3	78	7
	Other Eastern Europe	54	7	39	0
Latin America		67	9	23	1
Africa		66	9	24	0
Middle East		82	3	16	0

Source: Baron et al. (2007)

Annex 2. Example of a Waste Acceptance Decision Chart



HHV: Higher heating (calorific) value

(*) CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3

Source: GTZ/Holcim (2006)

Revision date: 22/03/2010

Annex 3. Compilation of Performance Verification and Test Burns Results in Cement Kilns (Karstensen, 2009c)

Introduction

2. 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) (as cited in Karstensen, 2009c) 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 % and better.

205. 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) (as cited in Karstensen, 2009c) 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), as cited in Karstensen (2009c)).

Results from trial burns conducted in the 1970s

206. 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 %. 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.

207. 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 % was determined for methylene chloride and a DRE greater than 99.9998 % was demonstrated for trichloroethylene.

Results from trial burns conducted in the 1980s

208. 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 %. DREs less than 99.99 % 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 %

Results from trial burns conducted in the 1990s

209. 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.

210. 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 % for carbon tetrachloride and greater than 99.995 % 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 % for carbon tetrachloride and greater than 99.996 % for trichlorobenzene.

211. 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 % were obtained in every case.

212. 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 % for all the introduced pesticides.

Results from recent trial burns

213. 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 %.

214. 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% at the highest PCB feeding rate.

215. 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 $\mu g/Nm^3$) 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 % achieved with the highest feeding concentration is probably higher in reality.

216. 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/m^3.

Summary

217. Earlier data which indicated cement kiln DRE results below 99.99 % 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.

218. 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.

Early applications of trial burn rules to cement kiln evaluation

219. 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.

220. 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
	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

Revision date: 22/03/2010

Site	POHC or waste component	DRE
	Trichloroethylene	99.997-99.9999
	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->99.9993
	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) (as cited by Karstensen, 2009c)

221. It should be noted that the DRE calculations did not include corrections for test compounds measured during baseline tests.

222. 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.

223. 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 completely destroyed by a combination of pyrolysis and oxidation.

Annex 4. Sources of Air Emissions

Particulate Matter

3. 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/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).

224. Outdated air pollution control equipment may emit up to several 100 mg/Nm^3. EPS easily reach < 50 mg/Nm^3. Fabric filters produce values < 20 mg/Nm^3. The visibility limit for point source dust is generally assumed to be around 80 mg/Nm^3.

Sulphur Oxides

225. 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.

226. Range of emissions depends on content of volatile sulphur compounds in raw materials: mostly below 300 mg/Nm^3; sometimes up to 3000 mg/Nm^3.

Nitrogen Oxides

227. There are four mechanisms of NO_X formation in cement kilns of which thermal and fuel NO_X formation are the most important. Thermal NO_X results from the oxidation of molecular nitrogen in air at high temperature. This phenomenon occurs in and around the flame in the burning zone of a cement kiln at a temperature greater than 1200ºC. Fuel NO_X 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 NO_X often exceeds that of thermal NO_X at these locations. The generation of feed NO_X has been demonstrated only in the laboratory by heating nitrogen-containing cement raw materials to the range of 300-800ºC in the presence of oxygen. Slow heating, such as occurs in wet and long-dry kilns, appears to increase the yield of NO_X for a given raw material. The yield of feed NO_X is potentially lower when the raw material is heated quickly in a preheater or precalciner system. Prompt NO_X is generated by the reaction of certain fuel-derived radicals with elemental nitrogen in a hydrocarbon flame and is a minor contributor to overall NO_X generation.

228. Range of emissions (unabated) is 300 to 2000 mg/Nm^3.

Carbon Oxides

229. 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, and/or 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 NO_X control strategy, CO sometimes is generated in the pyroprocess and may appear in the flue gas discharge if it is not somehow oxidized following its formation.

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

Organic Emissions

231. VOCs are organic compounds that generally contain from one to seven carbon atoms in the respective molecules and are a subset of total hydrocarbons (THCs) emissions from cement kilns. VOC emissions from cement kilns are of interest because of their involvement in the formation of atmospheric ozone and the designation of some VOCs as HAPs. THCs are primarily generated as a result of evaporation and/or cracking of the constituents of petroleum and kerogens found in the raw material mix. 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.

232. Range of emissions is dependant on content of raw materials of volatile organics: mostly below 50 mg/Nm^3; sometimes up to 500 mg/Nm^3.

Acid Gases

233. 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.

234. If fluorine is naturally present in the raw materials or added as a mineralizer, the emission of HF from a cement kiln system is also a possibility.

235. The mechanism for the formation of HCl 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.

236. Range of HCl emissions: SP/PC[9] kiln systems, <10 mg/Nm^3; wet kilns, up to 80 mg/Nm^3.

---

[9] SP = Suspension Preheater kiln; PC = Precalciner kiln

Ammonia

237. Trace quantities of NH_3 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 with regard to their potential contribution to regional haze. In addition, atmospheric reactions occur just outside of the stack between NH_3 and the oxides of sulphur or HCl that produce ammonium sulphate, ammonium bisulphate, or ammonium chloride as very fine particulate matter (PM). 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.

238. Range of emissions is <1 to 15 mg/Nm^3 as a rule with exceptions up to 40 mg/Nm^3.

Benzene

239. Benzene might be present in conventional and alternative raw materials and is partially roasted off at material preheating.

240. Range of emissions, normally 1 to 2 mg/Nm^3; up to 3 and more mg/Nm^3 in rare cases

Heavy Metals

241. 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.

242. 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 limit values (0.05 mg/Nm^3 for the European Union) in case of excessive inputs with materials.

Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans

243. Dioxins, furans or advanced precursors might be present in conventional (rarely) and alternative raw materials and 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 200º C to 450º C.

244. A comprehensive survey of PCDD/PCDF emissions from cement kilns in developed and developing countries is given in a report by Karstensen (2006b).

245. In a survey performed by CEMBUREAU, PCDD and PCDF measurements from 110 cement kilns in 10 countries were presented. The countries covered by the survey were Czech Republic, Denmark, France, Germany, Hungary, Italy, the Netherlands, Norway, Spain and the United Kingdom. The average concentration, taking into account all of the data in this dataset, was 0.016 ng I-TEQ/m^3. The range between the lowest and highest concentrations measured was < 0.001 to 0.163 ng I-TEQ/m^3. All measurements were expressed corrected to standard conditions (dry gas, 273 K, 101.3 kPa and 10% O_2).

246. 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/Nm^3 (71 kilns) and 0.030 ng TEQ/Nm^3 (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/Nm^3.

247. The PCDD/PCDF data presented by Karstensen (2006b) shows that:

- Most cement kilns can meet an emission level of 0.1 ng TEQ/Nm^3 if primary measures are applied;
- Co-processing of AFR, fed to the main burner, kiln inlet or the precalciner does not seem to influence or change the emissions of POPs;
- Data from dry preheater and precalciner cement kilns in developing countries show emission levels much lower than 0.1 ng TEQ/Nm^3.

Polychlorinated Biphenyls and Hexachlorobenzene

248. 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 µg PCB /Nm^3; 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/m^3 and HCB emissions below the detection limit of 31 ng/m^3.

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

Annex 5. Example of Emission Limit Values for Cement Kilns Co-processing Hazardous Waste (South African Government Department for Environmental Affairs and Tourism, 2009)

Emissions	Air emission standard (a)
PM (Total particulate matter)	30 (b) - 80 (c)
TOC	10 (d)
HCl	10
HF	1
SO_2	50 (d)
NO_X	500 (e)
Hg	0,05
Cd, Tl (Sum total)	0,05
Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V (Sum total)	0,5
PCDD/PCDF (ng/Nm^3 1-TEQ)	0,1

(a) Concentration expressed as mg/Nm^3 (daily average) unless otherwise stated, and at normalized conditions of 10% O_2, 101,3 kPa 273K/ 0ºC, dry gas.

(b) PM limit for (i) new kilns co-processing AFR, and for (ii) existing kilns co-processing AFR within 10 years of promulgation of the policy.

(c) PM limit (effective after 3 years of promulgation of the policy) for existing kilns co-processing AFR (excluding POPs waste), provided that current particulate emissions (as established through baseline monitoring) are not increased by the introduction of AFR

(d) Limits for TOC or SO_2 do not apply where elevated emissions result from conventional fuels or raw material, i.e. not from the co-processing of AFR provided that current TOC and SO_2 emissions (as established through baseline monitoring) are not exceeded the introduction of AFR.

(e) NOx limit for (i) new kilns co-processing AFR, and for (ii) existing kilns co-processing AFR (excluding POPs waste), within 10 years of promulgation of the policy, provided that current NOx emissions (as established through baseline monitoring) are not increased by the introduction of AFR.

4. All emission monitoring results must be reported as a daily average concentration expressed as mg/Nm^3, or ng/Nm^3 1-TEQ for PCDD/PCDF, and at normalized conditions of 10% O_2, 101,3 kPa, 273 K, dry gas.

249. Exit gas temperatures must be maintained below 200 ºC.

250. Pollution control devices (exhaust gas cooling and bag filter or ESP) must have a daily availability of 98% (i.e. maximum downtime of 2% or 30 minutes per running 24 hours). The cumulative annual downtime (total downtime over a one year period) may however not exceed 60 hours (0,685 % per annum).

251. Continuous, on-line measurement of the following emissions and operating parameters is required: Particulate matter (total particulate); O_2; CO; NO_X; SO_2; HCl; HF; VOC/TOC; emission exhaust volume (e.g. Nm^3/h) and flow rate (e.g. m/s); water vapour content of exhaust gas (humidity); exhaust gas temperature; internal process temperature(s); pressure; and availability of air pollution control equipment (including exit gas cooling).

252. Appropriate installation and functioning of automated, continuous, monitoring equipment for emissions to air; which are subject to quality control and to annual surveillance test. Independent calibration must be undertaken by means of parallel measurements with the reference methods at least every three years.

253. Periodic measurements of heavy metals and dioxin and furan emissions must be undertaken, using national (if available) or internationally acceptable methods, by independent/external, accredited specialists twice during the first 12 months of AFR co-processing, and annually thereafter.

254. Average emission values for heavy metals to be measured over a minimum sample period of 60 minutes to obtain arepresentative sample, and a maximum of 8 hours, and the average values for dioxins and furans (expressed as 1-TEQ) over a sample period of a minimum of 60 minutes and a maximum of 8 hours.

255. Periodic measurements of heavy metals and dioxins and furans are to be carried out representatively to provide accurate and scientifically correct emission data and results, and sampling and analysis must be carried out by independent accredited laboratories.

256. To ensure valid monitoring results are obtained, no more than five half-hourly average values in any day, and no more than ten daily average values per year; may be discarded due to malfunction or maintenance of the continuous measurement system.

257. Treatment of High Level POPs Containing Waste (as defined by the Stockholm and Basel Conventions) are to be preceded by an independently monitored Performance Verification Test to determine the DE and DRE of principal organic hazardous compounds (POHC) using a suitable verification compound (e.g. trichloroethane).

258. A detailed, independent report documenting and interpreting the results of the Performance Verification Test must be compiled. As a minimum a DE/DRE of 99.9999% would be required, as well as compliance with Air Emission Standards.