



**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



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MAY 2007, GENEVA, SWITZERLAND

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■ Summary

The main purpose of cement kilns is clinker production. Firing wastes in cement kilns aims at energy recovery and substitution of fossil fuels or substitution of minerals. In some cases hazardous wastes are disposed of in these installations.

The manufacturing process includes the decomposition of calcium carbonate (CaCO_3) at about 900°C to calcium oxide (CaO , lime) (calcination) followed by the clinking process at about 1450°C in a rotary kiln. The clinker is then ground together with gypsum and other additives to produce cement. According to the physical and chemical conditions the main process routes for the manufacture of cement are termed dry, wet, semi-dry and semi-wet.

The combustion process in the kiln, has the potential to result in the formation and subsequent release of chemicals listed in Annex C of the Stockholm Convention. In addition, releases from storage sites may occur.

Well-designed process conditions, and the installation of appropriate primary measures, should enable cement kilns firing hazardous waste to be operated in such a manner that the formation and release of chemicals listed in Annex C can be minimized sufficiently to achieve concentrations of PCDD and PCDF in flue gases of $<0.1 \text{ ng I-TEQ/Nm}^3$ (oxygen content 10%), depending on such factors as the use of clean fuels, waste feeding, temperature and dust removal. Where necessary, additional secondary measures to reduce such emissions should be applied.

Many data on PCDD/PCDF emissions to air are available

PCDD/PCDF releases via cement kiln dust and possibly clinker have been reported and are currently under further investigation. Data on PCB and HCB releases are still scarce

The performance levels associated with best available techniques and best environmental practice for control of PCDD/PCDF in flue gases are $<0.1 \text{ ng I-TEQ/Nm}^3$ with reference conditions of 273 K, 101.3 kPa, 10% O_2 and a dry gas basis.

Preamble

The following draft guidelines provide guidance on best available techniques and guidance on best environmental practices for cement kilns firing hazardous waste relevant to Article 5 and Annex C, Part II of the Convention. Waste may be co-processed in cement kilns either as alternative fuel or for destruction purposes. Therefore this section also considers the requirements of Article 6 of the Convention regarding destruction of wastes containing persistent organic pollutants.

In this section consideration is also given to the *General Technical Guidelines for the Environmentally Sound Management of Wastes Consisting of, Containing or Contaminated with Persistent Organic Pollutants (POPs)* developed by the Parties to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal (Basel Convention Secretariat 2005). Those guidelines give guidance

on the best available techniques to be applied to the destruction or irreversible transformation of persistent organic pollutants and identify cement kiln co-incineration as a process that can be used for such destruction and irreversible transformation of persistent organic pollutants in waste.

Destruction and co-incineration of wastes and hazardous wastes in cement kilns also fall within the scope of this section. It should be kept in mind when reading these guidelines that stringent definitions of the terms “waste” and “hazardous waste” do not currently exist. In the context of this guideline the term “waste” is used independent of its calorific value or its potential to substitute mineral resources.

This section addresses the issues arising from source categories in Annex C part II b: cement kilns firing hazardous wastes; and in the case of co-incineration in cement kilns of municipal wastes or sewage sludge, source category part II a.

1. Introduction

1.1 Cement industry in general

Global production of cement has consistently risen in past years, and this trend is forecast to continue. According to investigations by the cement industry, worldwide cement production in 2003 was 1,940 million tons, increasing from an estimated 1,690 million tons in 2001 and 1,660 million tons in 2002. A large part of the production is based on dry processes (de Bas 2002; DFIU/IFARE 2002).

Over the last years there has been a steady annual increase of an estimated 3.6% due to the strong demand in developing countries and countries with economies in transition. At present, of total global output, Europe has a share of 14.4%, United States of America 4.7%, rest of America 6.6%, Asia 67.5% (China 41.9%), Africa 4.1% and the rest of the world 2.7%. Cement consumption globally was estimated to be an average 260 kg per capita in 2004 (Cembureau 2004).

Cement production in Europe amounts to about 190 million tons per year. More than 75% of this output is based on dry processes, due to the increased adoption of these more energy-efficient processes for new and expanding facilities in recent years; 16% is based on semi-dry or semi-wet processes and 6% on wet processes. The typical capacity of a new European kiln is 3,000 tons of clinker per day (Wulf-Schnabel and Lohse 1999).

The Chinese cement industry produced 1,038 million tons of cement in 2005 (808 kg per capita; 45.4% of world production)¹. Approximately 60% was produced in 4,000 vertical shaft kilns (Karstensen 2006a).

In the United States the average kiln produces 468,000 tons per year (2002 figures). Currently, about 81% of the cement produced in the United States is manufactured using dry process technology (Portland Cement Association website).

Traditionally, the primary fuel used in cement kilns is coal. A wide range of other fuels is or has been also used, including petroleum coke, natural gas and oil (European

Commission 2001). In Europe the specific energy consumption of the cement industry has been reduced by about 30% over the past 20 years (equivalent to approximately 11 million tons of coal per year) (Cembureau 2004). It is not uncommon for kilns to be capable of multifuelling and for fuels to be changed from time to time based on the prevailing costs of different fuels.

1.2 Firing of waste in cement kilns

In addition to conventional fuels mentioned in section 1.1, the cement industry uses various types of waste as a fuel. In the European cement industry the consumption of waste as a fuel amounts to about 6 million tons, which corresponds to a thermal substitution rate of 18% (Cembureau 2004).

Furthermore, cement kilns can contribute to the destruction of waste, including hazardous waste, some with little or no useful energy or mineral content. This may be done at the request of national governments or in response to local demand. In a well-controlled facility high destruction efficiency of organic compounds present in such wastes can be achieved.

This co-processing of hazardous waste can only be done if certain requirements with respect to input control (for example of heavy metal content, heating value, ash content, chlorine content), process control and emission control are met, as outlined below.

However, it must be reiterated that cement kilns are primarily production processes for clinker, and not all operating conditions that may produce satisfactory clinker product are ideal for the destruction of wastes; for example, cement kilns tend to operate at lower exhaust oxygen levels and more elevated carbon monoxide levels than well-operated incinerators. Destruction of organic wastes requires not only high temperature and long residence time, but also the availability of adequate oxygen and sufficient mixing between the organic compounds intended for destruction and the oxygen. Conditions can arise where wastes are not destroyed adequately if waste is not introduced properly to the kiln or available oxygen levels are too low. Good design and operation are critical to the use of cement kilns for this application.

It should be emphasized that this activity is distinct from fuel or raw material substitution in the process. Cement kilns have been used in this way for many years in countries such as Japan, Norway and Switzerland, where there is little space for landfill sites. More recently, modern kilns have been used for waste destruction in some developing countries where the lack of existing waste disposal and incineration infrastructure means that kilns are the most economical and readily available option. This section aims to give guidance with respect to environmental issues that may arise in such instances. Even where good waste disposal infrastructure exists, it may be useful to supplement local capacity through use of cement kilns.

Application of approaches involving waste management, such as recycling or reprocessing, is preferable to disposal by landfill or dumping or destruction of waste in cement kilns. A case-by-case evaluation should be carried out in the context of an overall waste management strategy (see section III C (ii)).

In exceptional cases cement kilns can be used for the safe disposal of wastes that have little calorific or mineral value and do not contribute to the clinker production process. For this type of treatment, regulatory authorities and cement plant operators must come to individual agreements on a case-by-case basis.

Where cement kilns are used for the destruction of wastes, alternative disposal routes should be carefully assessed. Waste destruction in cement kilns must meet strict environmental, health and safety standards, and must not impair the quality of the final product. In countries where stringent requirements for the final product do not exist it is more important to require application of best available techniques and best environmental practices for those installations co-incinerating wastes. The process must be precisely controlled when destroying such wastes, and emissions regularly measured.

2. Links to other relevant information

Comprehensive background information on cement kiln operation in general and on the firing of waste in cement kilns can be found in:

European Commission.2001. *Reference Document on the Best Available Techniques in the Cement and Lime Manufacturing Industries*. BAT Reference Document (BREF). European IPPC Bureau, Seville, Spain².(<http://eippcb.jrc.es/pages/FActivities.htm>)

European Commission.2005. *Reference Document on the Best Available Techniques for the Waste Treatments Industries*. BAT Reference Document (BREF). European IPPC Bureau, Seville, Spain.(<http://eippcb.jrc.es/pages/FActivities.htm>)

Holcim. 2006. *Guidelines on Co-Processing Waste Materials in Cement Production*.The GTZ- Holcim public private partnership 2006. (http://www.holcim.com/gc/CORP/uploads/GuidelinesCOPROCEM_web.pdf)

CSI (Cement Sustainability Initiative). 2006. *Guidelines for the Selection and Use of Fuels and Raw Materials in the Cement Manufacturing Process: Fuels and Raw Materials*. World Business Council for Sustainable Development, Geneva, Switzerland. (http://www.wbcscement.org/pdf/tf2/tf2_guidelines.pdf)

2.1 General waste management considerations (Section III.C (ii))

Society can manage wastes in a number of ways, depending on their physical and chemical nature, and on the economic, social, and environmental context in which they are produced. Some of these are listed below. Specific decisions will always be influenced by local circumstances such as the availability of waste treatment facilities, alternative markets for materials, and the infrastructure available to safely collect, manage and transport waste materials (CSI 2005). Section III C (ii) of these Guidelines, shows a hierarchy of decision-making for waste management.

2.2 Other options for treatment of waste

The use of cement kilns for the treatment of waste should be considered only as part of the general context of waste management options in a hierarchy such as that

illustrated above. Waste incineration is also an option for disposal of wastes and the guidelines for best available techniques and best environmental practices for this source category should be considered when cement kilns are used in this application.

2.3 Basel Technical Guidelines

Technical Guidelines developed by the Basel Convention have to be given careful consideration as they provide guidance on best available techniques to be applied to the destruction or irreversible transformation of persistent organic pollutants as wastes.

3. Cement production processes

In this guideline the description of the cement production process is limited to the various rotary kiln process routes. It has to be kept in mind that in China most cement is produced in vertical shaft kilns which show low energy efficiency and poor environmental performance (H. Klee, World Business Council for Sustainable Development, personal communication 2004). Therefore, vertical shaft kilns should not be considered as an option for best available techniques..

3.1 General principles

The basic chemistry of the cement manufacturing process begins with the decomposition of calcium carbonate (CaCO_3) at about 900°C to leave calcium oxide (CaO, lime) and liberate gaseous carbon dioxide (CO_2); this process is known as calcination. This is followed by the clinkering process in which the calcium oxide reacts at high temperature (typically $1,400^\circ\text{C} - 1,500^\circ\text{C}$) with silica, alumina and ferrous oxide to form the silicates, aluminates and ferrites of calcium that comprise the Portland clinker. This clinker is then ground together with gypsum and other additives to produce cement. Figure 1 identifies the principal processes and system boundaries of cement production.

3.2 Preparation of raw materials

Preparation of the raw material is of great importance to the subsequent kiln system both in getting the chemistry of the raw feed right and in ensuring that the feed is sufficiently fine. Accurate metering and proportioning of the mill feed components by weight is important for achieving a consistent chemical composition. This is essential for steady kiln operation and a high-quality product.

Solid fuel preparation (crushing, grinding and drying) is usually carried out on site.

The raw materials, in controlled proportions, are ground and mixed together to form a homogeneous blend with the required chemical composition. For dry and semi-dry kiln systems, the raw material components are ground and dried to a fine powder, making use mainly of the kiln exhaust gases and/or cooler exhaust air. For raw materials with a relatively high moisture content, and for start up procedures, an auxiliary furnace may be needed to provide additional heat.

Wet grinding is used only in combination with a wet or semi-wet kiln system. The raw material components are ground with added water to form a slurry. The wet process is normally preferred whenever the raw material has a moisture content of more than 20% by weight.

■ **Figure 1. Process identification and system boundaries of cement production**

Source: European Commission 2001

3.3 The rotary kiln processes

The raw feed material, known as raw meal, raw mix, slurry (with a wet process) or kiln feed, is heated in a kiln, typically a large, inclined, rotating cylindrical steel furnace (rotary kiln). Kilns are operated in a countercurrent configuration. Gases and solids flow in opposite directions through the kiln, providing for more efficient heat transfer. The raw meal is fed at the upper or cold end of the rotary kiln, and the slope and rotation cause the meal to move toward the lower or hot end. The kiln is fired at the hot end, usually with coal or petroleum coke as the primary fuel. As the meal moves through the kiln and is heated, it undergoes drying and pyroprocessing reactions to form the clinker, which consists of lumps of fused, incombustible material. There are several ways of introducing the fuels (both fossil and alternative) into the kiln. This is described in more detail in paragraph 4.1 below.

The clinker leaves the hot end of the kiln at a temperature of about 1,000°C. It falls into a clinker cooler, typically a moving grate through which cooling air is blown.

Various process routes for the manufacture of cement can be followed during the pyroprocessing step to accomplish the required physical and chemical transformations. They vary with respect to equipment design, method of operation and fuel consumption.

3.3.1 The dry process

In the dry process, the raw materials are ground and dried to raw meal in the form of a flowable powder. The dry raw meal is fed to the preheater or precalciner kiln or, more rarely, to a long dry kiln. The energy efficiency of the kiln is higher if the raw meal is preheated before it enters the kiln.

3.3.1.1 The preheater dry process

In this process preheaters are used to increase the thermal efficiency. A raw meal preheater consists of a vertical tower containing a series of cyclone-type vessels. Raw meal is introduced at the top of the tower. Hot kiln exhaust gases pass countercurrent through the downward moving meal to heat the meal prior to introduction into the kiln. The meal is separated from the kiln flue gases in the cyclone, and then dropped into the next stage. Because the meal enters the kiln at a higher temperature than with conventional long dry kilns, the length of the preheater kiln is shorter.

With preheater systems, it is sometimes necessary to remove undesirable components, such as certain alkali constituents, through an alkali bypass system located between the feed end of the rotary kiln and the preheater tower. Otherwise, these alkali constituents may accumulate in the kiln, and removal of the scale that deposits on vessel walls is difficult and may require kiln shutdown. This problem can be reduced by withdrawing a portion of the gases with a high alkali content. If this alkali bypass has a separate exhaust stack it can be expected to carry and release the same pollutants as the kiln exhaust.

3.3.1.2 The preheater/precalciner dry process

This process is similar to the preheater dry process, with the addition of an auxiliary firing system to increase the raw materials temperature prior to introduction into the kiln (Figure 2). A precalciner combustion vessel is added to the bottom of the preheater tower. The primary advantage of using the precalciner is that it increases the production capacity of the kiln, as only the clinker burning is performed there. Use of the precalciner also increases the kiln refractory lifetime due to reduced thermal load on the burning zone. This configuration may also require a bypass system for alkali control, which, if released from a separate exhaust stack, can be expected to carry and release the same pollutants as the kiln exhaust.

■ Figure 2. Rotary kiln with suspension preheater and calciner

Note: ESP = electrostatic precipitator (dust collection device).

3.3.2 The semi-dry process

In the semi-dry process dry raw meal is pelletized with 12–14% water and fed into a grate preheater before the kiln or to a long kiln equipped with crosses, on which the pellets are dried and partially calcined by hot kiln exhaust gases before being fed to the rotary kiln.

3.3.3 The semi-wet process

In the semi-wet process the raw materials (often with high moisture content) are ground in water to form a pumpable slurry, which is then dewatered in filter presses. The filter cake is extruded into pellets and fed either to a grate preheater or directly to a filter cake dryer for raw meal production.

3.3.4 The wet process

In the wet process, the raw materials (often with high moisture content) are ground in water to form a pumpable slurry. The slurry is either fed directly into the kiln or first to a slurry dryer. The wet process is an older process used in the case of wet grinding of raw materials. It results in a higher energy demand compared to the dry process because of water evaporation from the slurry.

3.4 The cement grinding process

The clinker is ground with gypsum and other additives, usually in a ball mill, to produce the final product – cement. The cement is conveyed from the finish cement mill to large, vertical storage silos in the dispatch or shipping department. Cement is withdrawn from the cement storage silos by a variety of extracting devices and conveyed to loading stations in the plant or directly to transport vehicles.

3.5 Emission control

In general, modern cement kilns are equipped with either electrostatic precipitators or fabric filters, or both, for particulate matter control. In some cases, the flue gases are cooled prior to the dry air pollution control device. Acid gas pollution control devices have not been used at cement kilns as the raw materials are highly alkaline and provide a significant degree of acid gas control (Karstensen 2006b), although there are a number of kilns equipped with wet scrubbers, if the sulphur content of the raw meal is high.

Techniques for reduction of NO_x are mainly primary integrated methods like flame cooling, burner design, staged combustion or selective non-catalytic reduction by ammonia injection.

4. Burning

4.1 Operation with conventional fuels

Conventional fuels used in cement plants are fossil fuels such as coal, lignite, fuel oil or natural gas. These fuels can be used singly or in combination, in which case a minimum quality (in terms of heating value, heavy metal or sulphur content) must be ensured. Some of the fossil fuels (e.g. coal) are ground in mills before they are injected.

For smooth kiln operation, the production of a homogeneous clinker and complete combustion, some important criteria have to be considered for conditioning of the fuels. The oxidation of the fuel constituents occurs more quickly when the fuels are well mixed and the specific surface is larger. In the case of liquid fuel, injection has to be as smooth as possible. In the case of solid fuels, thorough mixing with other fuels used at the same time is required. This is not necessarily required as long as the material is homogenous and highly uniform.

A cement plant consumes 3,000 to 6,500 MJ (electricity and transport not included) per ton of clinker produced, depending on the raw materials and the process used. 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 burn to leave fuel ash containing silica and alumina compounds (and other trace elements). These combine with the raw materials in the kiln, contributing to the structure of the clinker and forming part of the final product. Energy use typically accounts for 30–40% of the production costs. The different types of fuels, in decreasing order of importance, are:

- Pulverized coal and petroleum coke (petcoke);
- (Heavy) fuel oil;
- Natural gas.

Potential feed points for supplying fuel to the kiln system are via:

- The main burner at the rotary kiln outlet end;
- A feed chute at the transition chamber at the rotary kiln inlet end (for lump fuel);

- Secondary burners to the riser duct;
- Precalciner burners to the precalciner;
- A feed chute to the precalciner/preheater (for lump fuel);
- A mid-kiln valve in the case of long wet and dry kilns (for lump fuel).

Depending on operational conditions – explicitly in the case of improper operation of the installation – significant emissions of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) can occur. In proper operation the release of PCDD/PCDF should be well below 0.1 ng TEQ/m³.

4.2 Firing of waste or hazardous waste

The selection of wastes and materials is driven by a number of additional interrelated considerations, including:

- Impact on CO₂ emissions and fuel consumption;
- Impact on fuel cost;
- Impact on other emissions such as NO_x, SO₂, particulates, other persistent organic pollutants, heavy metals, CO, organic substances;
- Impact on mining and quarry activity;
- Stability of kiln operation (affected by parameters such as heating value and water content);
- Impact of product quality (e.g. restriction of the chlorine content in cement: <0.1%).

The requirements of product quality, particularly the restriction of the chlorine content of cement to 0.1%, limits firing options, and the chlorine input has to be monitored.

4.2.1 Examples of waste and alternative fuels

The substitution of fossil fuels with alternatives is a well-developed practice in a number of countries. Some countries have been using wastes as alternative fuels for almost 30 years, and some national governments actively promote this approach, provided that stringent requirements with regard to input, process and emission control are met. However, some stakeholders and other jurisdictions have viewed the practice in the same light as incineration. In the countries where this practice is well established, consideration has been given to the types of materials best suited to use in cement kilns (CSI 2005), which may include:

- Used tires;
- Meat, bone meal and animal fat;
- Plastics;
- Impregnated sawdust;

- Wood, paper, cardboard, packaging waste;
- Sludge (paper fibre, sewage);
- Agricultural and organic waste;
- Shale, oil shales;
- Coal slurries;
- Distillation residues;
- Fine fractions of coal or coke /anodes/chemical cokes;
- Waste oils, oiled water;
- Spent solvents.

It is important to control waste parameters (e.g. heat value, water content, ash content, content of chlorine, content of heavy metals).

4.2.2 Negative waste list

Co-processing should only be applied if not just one but all tangible preconditions and requirements of environmental, health and safety, socio-economic and operational criteria are fulfilled. As a consequence not all waste materials are suitable for co-processing. The following is a list of waste not recommended for co-processing in cement plants:

- Nuclear waste;
- Electronic waste;
- Explosives;
- Mineral acids;
- Asbestos-containing waste;
- High-concentration cyanide waste;
- Infectious medical waste;
- Chemical or biological weapons destined for destruction;
- Entire batteries;
- Unsorted municipal garbage and other waste of unknown composition.

Electronic waste is composed of computer and accessories, entertainment electronics, communication electronics, toys and also white goods such as kitchen devices or medical apparatus. The average composition shows that electronic waste contains, on the one hand, substances harmful to health and the environment such as Cl, Br, P, Cd, Ni, Hg, PCB and brominated flame retardants in high concentrations, often higher than threshold limit values. On the other hand, electronic waste contains such a high scarce precious metal content that all efforts have to be undertaken to recycle it. Co-processing

of the plastic parts of electronic waste would be an interesting option, but requires disassembling and segregation first (after Holcim, 2006).

The list outlined above is not an exhaustive list. In general, wastes with a low heat value and a very high heavy metal content are not suitable for being inserted into a cement kiln. Municipal solid waste should not be co-incinerated in cement kilns due to its unpredictable composition and its characteristics. Furthermore, individual companies may exclude additional materials, depending on local circumstances.

4.2.3 Considerations for selection of wastes

The selection of wastes is a complex process and is influenced by many factors, such as kiln operation, the nature of the waste itself, the general impact on the environment, the desired clinker quality and the probability of the formation and release of chemicals listed in Annex C of the Stockholm Convention and other releases into the environment. The operator should develop a fuels evaluation and acceptance procedure. Based on this procedure an assessment is carried out of the effect of the fuel on plant emissions and the potential need for new equipment or procedures to ensure that there is no negative impact on the environment.

The variables that should be considered when selecting fuels and raw materials include (CSI 2005):

4.2.3.1 Kiln operation

- Chlorine, sulphur, and alkali content: These may build up in the kiln system, leading to accumulation, clogging and unstable operation; excess in chlorine or alkali may produce cement kiln dust or bypass dust (and may require installation of a bypass), which must be removed, recycled or disposed of responsibly;
- Water content: High water content may reduce the productivity and efficiency of the kiln system;
- Heat value (fuel): The heat value is the key parameter for the energy provided to the process;
- Ash content: The ash content affects the chemical composition of the cement and may require an adjustment of the composition of the raw materials mix;
- Additional factors are relevant, such as treatment capacity and volume of waste gas;
- Stability of operation (e.g. CO peaks) and the state (liquid, solid), preparation (shredded, milled) and homogeneity of the waste.

4.2.3.2 Clinker and cement quality

- Phosphate content: This influences setting time;
- Chlorine, sulphur, and alkali content: These affect overall product quality;

- Thallium and chromium: in relation to cement kiln dust and cement quality and possible allergic reactions in sensitive users.

4.2.3.3 Atmospheric pollutant emissions other than chemicals listed in Annex C

- High sulphur contents in raw materials and inserted fuels and wastes: These may result in the release of SO₂;
- Control of exhaust: Where an alkali bypass system is installed, appropriate control of the exhaust to atmosphere also needs to be provided on the bypass exhaust similar to that mandated for the main exhaust stack;
- Chlorides in raw materials or fuels: These may combine with alkalis also present in the feed 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 in fuel or raw material: Raw materials and fuels will always contain metals in varying concentrations. The behaviour of these metals in the burning process is dependent on their volatility. Nonvolatile metal compounds remain within the process and exit the kiln as part of the cement clinker composition. Semi-volatile metal compounds are partly taken into the gas phase at sintering temperatures to condense on the raw material in cooler parts of the kiln system. This leads to a cyclic effect within the kiln system (internal cycles) which builds up to the point where an equilibrium is established and maintained between input and output via the cement clinker. Volatile metal compounds condense on raw material particles at lower temperatures and potentially form internal or external cycles, if not emitted with the flue gas of the kiln. Thallium and mercury and their compounds are particularly easily volatilised and to a lesser extent so are cadmium, lead, selenium and their compounds. (European Commission 2001).
- The metal concentration in cement kiln dust depends on the feedstock and recirculation in the kiln system. In particular, the use of coal and waste fuels may increase the input of metals into the process. Dust control devices can only capture the particle-bound fraction of heavy metals. The retention rate for the gaseous fraction of volatile metals such as mercury is low. Such inputs into the kiln system should therefore be limited. This needs to be taken into account as soon as wastes containing volatile heavy metals such as mercury, lead or cadmium are co-incinerated. Wood treated with copper, chromium, arsenic etc. also requires special consideration with regard to the efficiency of the flue gas cleaning system.
- The choice of fuels can also affect greenhouse gas emissions. For example, substituting fossil fuels by biomass results in a decrease of net CO₂ emissions;
- Wastes may influence NO_x emissions, depending on their composition and water content.

4.2.4 Analysis of input streams

The kiln operators should develop criteria for acceptance of raw materials including wastes and should carry out an ongoing evaluation procedure that includes the following features:

- Name and address of the deliverer/supplier, origin of the waste, volume, water and ash content, calorific value, concentration of chlorides, fluorides, sulphur and heavy metals;
- Each material supplier should be required to provide, initially and periodically thereafter, representative samples of the fuel, which will be used to evaluate the fuel before it is delivered to the plant;
- The supplier should also be required to include a datasheet detailing the chemical and physical properties of the fuel being supplied, and information on relevant health, safety and environmental considerations during transport, handling and use;
- The sample's physical and chemical characteristics should be tested and checked against specifications.

A clear system for the management of quality assurance and quality control has to be implemented, including periodic sampling and analysis of the materials actually delivered to the plant and verification that levels of contaminants of concern remain within the established specifications.

4.2.5 Pretreatment and storage for use of waste as alternative fuel

The storage requirements for waste depend on the type of materials. In general, care has to be taken to minimize emissions of pollutants, and to address technical and hygienic concerns.

As regards initial storage, materials strongly contaminated (e.g. with substantial biologic content) and high moisture (up to 40%) need to be stored in specially designed containers due to hygienic concerns. Animal meal has to be conditioned in absolutely closed systems. It is supplied in containers, and the material is conveyed either pneumatically or by mechanical equipment into storage. Liquid waste (waste oil, solvents) needs to be stored in special containers designed to resist leakage and explosion hazards. Special security precautions have to be developed and implemented (taking into account, for example, risk of explosion).

Intermediate storage at the conditioning plant aims at checking the quality of the waste-derived fuels after the preparation process. Here, containers are normally used.

Initial storage and preparation of different types of waste for use as fuel is usually performed outside the cement plant by the supplier or by waste treatment specialist organizations. Such centralized solutions can be of benefit to kiln operators, whose primary task is to produce clinker for cement production. However, due diligence mandates that such fuels should be subjected to quality assurance measures by the receiving facility. This means only the separated and pretreated waste fractions need to be stored at the cement plant and then proportioned for feeding to the cement kiln.

Since supplies of waste suitable for use as fuel tend to be variable whilst waste material markets are rapidly developing, it is advisable to design storage and preparation plants as multipurpose (Karstensen 2006b). Measures have been initiated (2003) in the European Union to standardize solid recovered fuels derived from non-hazardous waste.

Mixing of waste with the aim of meeting certain requirements, but resulting in concealment of environmental impact by dilution of concentrations, cannot be considered as acceptable practice.

4.2.6 Destruction efficiency

The co-processing of hazardous waste can only be done if certain requirements with respect to input control, process control and emission control are met. One of these process parameters is the oxygen content in the exhaust gases. Destruction of organic wastes requires not only high temperature and long residence time, but also the availability of adequate oxygen, proper introduction into the kiln of the organic compounds intended for destruction, and sufficient mixing of the compounds and the oxygen. Good design and operation are crucial to the use of cement kilns for this application.

Many cement kilns co-process waste commercially (i.e., they accept waste from off-site generators), in most cases for use as a fuel substitute in the production of Portland 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 it is introduced onto the feed shelf in the high-temperature section.

In the case of hazardous wastes, complete destruction of combustible toxic compounds such as halogenated organic substances has to be ensured. Wastes that are fed through the main burner will be destroyed in the primary burning zone at a flame temperature of $>1,800^{\circ}\text{C}$. Waste fed to a secondary burner, preheater or precalciner will be exposed to lower temperatures, though expected burning zone temperatures in the precalciner are typically $>1,000^{\circ}\text{C}$.

Volatile components in material that is fed at the upper end of the rotary kiln or as lump fuel can evaporate or evolve by pyrolysis and be released from the stack without being combusted, since kiln operation is countercurrent. Batch wastes injected at mid or feed-end locations do not experience the same exceptionally elevated temperatures as do liquid wastes introduced at the hot end. In some situations, volatile organic compounds may be released from the charge so rapidly that they are not able to mix with oxygen and ignite before they cool below a critical temperature, forming products of incomplete combustion. CO sensors installed for process control can detect incomplete combustion and allow corrective measures to be undertaken.

The hazardous waste used as a fuel by the cement industry consists mainly of organic material, but may also contain varying amounts of metal components. To determine whether or not a cement kiln can burn hazardous waste fuel effectively, the fate of the organic constituents must be determined.

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. The destruction and removal efficiency for chemicals such as methylene chloride, carbon tetrachloride, trichlorobenzene, trichloroethane and polychlorinated biphenyls (PCB) has typically been measured at 99.995% and better (Karstensen 2006b).

The potential use of cement kilns to incinerate wastes containing PCB has been investigated in many countries. The destruction and removal efficiencies determined from several trial burns indicate that well-designed and operated cement kilns are effective at destroying PCB. A destruction and removal efficiency of 99.9999% is required by several jurisdictions (e.g. United States Toxic Substances Control Act, Canadian Federal Mobile PCB Treatment and Destruction Regulations) for the incineration of these compounds, which could be used as an indicative best available technique standard.

5. Process inputs and outputs

5.1 General outputs

The main environmental issues associated with cement production are emissions to air, energy use, and soil and groundwater contamination from the handling and storage of waste cement kiln dust. Wastewater discharges are usually limited to surface run-off and cooling water and generally do not contribute substantially to water pollution.

Primary process outputs of cement production are:

- Product: Clinker, which is ground and then mixed with other ingredients to produce cement;
- Kiln exhaust gas: Typical kiln exhaust gas volumes range between 1,700 and 2,500 m³/Mg of clinker (cubic metres per metric ton of clinker; reference conditions 101.3 kPa, 273 K, dry gas basis) for all types of kilns. Suspension preheater and precalciner kiln systems normally have exhaust gas volumes around 2,000 m³/Mg of clinker (dry gas, 101.3 kPa, 273 K);
- Cement kiln dust (collected in the air pollution control equipment): In the United States, some 64% of cement kiln dust is recycled back into the kiln and the remainder, which is generated at the rate of about 40 kg/ton of clinker, is primarily buried in landfills (WISE 2002; EPA 2000). Holcim, one of the world's largest cement producers, sold or landfilled 29 kg of cement kiln dust per ton of clinker in 2001 (Holcim website);
- Recycling cement kiln dust to the kiln generally results in a gradual increase in the alkali content of generated dust, which may lead to damage to kiln linings, produce inferior cement and increase both stack particle emissions (EPA 1998b) and the amount of cement kiln dust that must be disposed of and the resulting air emissions due to its handling and disposal (EPA 1998a). In Europe cement kiln dust is usually circulated back to the kiln feed material or added directly to the

product cement (Lohse and Wulf-Schnabel 1996). The build up of alkalis in the kiln system may be avoided by either removal of the collected kiln dust or by using an alkali bypass system. For preheater and precalciner kilns, this is sometimes accomplished by alkali bypass systems at the preheater tower that removes alkalis from the kiln system;

- 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 the United States Environmental Protection Agency, the pollutants in this gas stream are similar to those in the main kiln exhaust gases and similar pollution abatement equipment and monitoring is required (EPA 1999). An alkali bypass ratio of more than 10% is commonly required for alkali removal (Sutou, Harada and Ueno 2001). However, a bypass ratio of 30% has also been reported (Holsiepe, Shenk and Keefe 2001).

5.2 Energy use

The cement industry is an energy-intensive industry where energy typically accounts for 30–40% of operating costs (i.e., excluding capital costs). A cement plant consumes 3,000 to 6,500 MJ of fuel per ton of clinker produced. This large range of energy demand covers all kinds of cement kilns.

The theoretical energy use for the burning process (involving chemical reactions) is about 1,700 to 1,800 MJ per ton of clinker. The actual fuel energy use for different kiln systems is in the following ranges (MJ per ton of clinker)³:

- 3,000–3,800 for dry process, multistage cyclone preheater and precalciner kilns;
- 3,100–4,200 for dry process rotary kilns equipped with cyclone preheaters;
- 3,300–4,500 for semi-dry/semi-wet processes (Lepol kiln);
- Up to 5,000 for dry process long kilns;
- 5,000–6,000 for wet process long kilns;
- 3,100 to >6,500 for shaft kilns and for special cements.

The electricity demand is about 90–130 kWh per ton of cement (European Commission 2001).

To optimize the input of energy in existing kiln systems it is possible to change the configuration of the kiln to a short dry process kiln with multistage preheating and precalcination. This is usually only feasible as part of a major upgrade with an attendant increase of production.

Electrical energy use can be minimized through the installation of power management systems and the utilization of energy-efficient equipment such as high-pressure grinding rolls for clinker comminution and variable speed drives for fans.

Energy efficiency will generally be decreased by the addition of most types of end-of-pipe abatement, since their operation usually requires an increment in electrical energy

use. Some of the reduction techniques described below will have a positive effect on energy use, for example process control optimization.

Current estimates suggest that the cement industry can increase its energy efficiency by 0.5–2% per year by replacing old or outdated equipment. If new dry process plants replace older wet process units, significant energy efficiency gains are possible (CSI 2005).

5.3 Emissions of PCDD/PCDF

5.3.1 Formation of PCDD/PCDF

Any chlorine input in the presence of organic material may potentially cause the formation of PCDD and PCDF in heat (combustion) processes. PCDD/PCDF can be formed by the de novo synthesis mechanism in or after the preheater and in the air pollution control device if chlorine and hydrocarbon precursors are available in sufficient quantities in the temperature range 200° C to 450° C. A graph of the temperature profile for gases and materials and their typical residence times in each stage of a clinker kiln with cyclonic preheater and precalciner is shown in Figure 3 (Fabrellas et al. 2004).

■ Figure 3. Temperature profile and typical residence time stages of clinker kiln with cyclonic preheater and precalciner

Source: Fabrellas et al. 2004.

5.3.2 Studies on emissions of PCDD/PCDF into air

A comprehensive survey of PCDD/PCDF emissions from cement kilns in developed and developing countries is given in (Karstensen 2006). The data represents more than 2200 measurements in kilns with and without the firing of a wide range of waste materials and covering the period from early 1990'ies until recently. Table 1 summarizes the results of the PCDD/PCDF measurements; some examples are described in more detail hereunder.

■ Table 1. Summary of PCDD/PCDF measurement data

Country or company	Use of alternative fuel and raw materials?	Concentration, in ng I-TEQ/m ³ , of PCDD/PCDF ^a	Number of measurements	Emission factor µg I-TEQ/ton cement ^a
Australia	Yes	0.001–0.07	55	0.0032–0.216
Belgium	Yes	<0.1	23	
Canada	Yes	0.0054–0.057	30	
Chile	Yes	0.0030–0.0194	5	
Colombia	Yes	0.00023–0.0031	3	
Denmark	Yes	<0.0006–0.0027	?	
Egypt	Yes	<0.001	3	
Europe	Yes	<0.001–0.163	230	<0.001–5
Germany 1989–1996	Yes	0.02	>150	
Germany 2001	Yes	<0.065	106	
Holcim 2001	Yes	0.0001–0.2395	71	0.104 (clinker)
Holcim 2002	Yes	0.0001–0.292	82	0.073 (clinker)
Holcim 2003	Yes	0.0003–0.169	91	0.058 (clinker)
Heidelberg	Yes	0.0003–0.44	>170	
Japan	Yes	0–0.126	164	
Lafarge	Yes	0.003–0.231	64	
Mexico	Yes	0.0005–0.024	3	
Norway	Yes	0.02–0.13	>20	0.04–0.40
Philippines	Yes	0.0059–0.013	5	
Poland	Yes	0.009–0.0819	7	
Portugal		0.0006–0.0009	4	
RMC	Yes	0.0014–0.0688	13	
Siam Cement Co.	Yes	0.0006–0.022	4	
South Africa	(Yes)	0.00053–0.001	2	
Spain	Yes	0.00695	89	0.014464
Spain Cemex	Yes	0.0013–0.016	5	
Spain Cimpor	Yes	0.00039–0.039	8	
Taiheiyō	Yes	0.011	67	
Thailand	Yes	0.0001–0.018	12	0.00024–0.0045
UK	Yes	0.012–0.423	14	<0.025–1.2
Uniland		0.002–0.006	2	0.005–0.011
USA ^b	Yes	0.004– ~ 50	~ 750	<0.216–16.7
Venezuela	Yes	0.0001–0.007	5	
Vietnam		0.0095–0.014	3	

a. The numbers are either given as a range or as the mean value, and refer to 10 or 11% O₂, depending on national regulations.

b. The high numbers from the United States relate to measurements obtained in the 1990s; the number of measurements is approximate.

Source: Karstensen 2006b.

In a recent 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/m³. The range between the lowest and highest concentrations measured was <0.001 to 0.163 ng I-TEQ/m³ (Karstensen 2006b). All measurements were expressed corrected to standard conditions (dry gas, 273 K, 101.3 kPa and 10% O₂).

The Holcim Cement Company operates cement kilns worldwide. A recent report from Holcim gives average PCDD/PCDF values for 2001 and 2002 as 0.041 ng TEQ/Nm³ (71 kilns) and 0.030 ng TEQ/Nm³ (82 kilns) respectively. Of these measurements, 120 were from countries within the Organisation for Economic Co-operation and Development (OECD), with an average value of 0.0307 ng TEQ/Nm³; the minimum and maximum values measured were 0.0001 and 0.292 ng TEQ/Nm³ respectively, with nine long wet kilns being above 0.1 ng TEQ/Nm³. For the 29 measurements from non-OECD countries, the average value was 0.0146 ng TEQ/Nm³; the minimum and maximum values measured were 0.0002 and 0.074 ng TEQ/Nm³ respectively, with no measurements being above 0.1 ng TEQ/Nm³ (Karstensen 2006b). Table 1 above summarizes the results of the PCDD/PCDF measurements.

Experience has shown that, with relatively high temperatures in the electrostatic precipitator and the use of raw material with high organic content, high levels of emissions of chemicals listed in Annex C are possible.

PCDD/PCDF emissions in 2004 from a long dry kiln in the UK reached 136 ng TEQ/m³ and averaged more 50 ng TEQ/m³ over the year with total emissions of more than 40 g TEQ. The kiln, now closed, was operating with relatively high temperatures in the electrostatic precipitator and used raw material with high organic content together with waste pulverised fuel ashes⁴.

Data from several kilns in the United States show PCDD/PCDF emissions of 1.76 ng I-TEQ/m³ when operating their air pollution control devices in the range of 200°C – 230°C.⁵ Tests in the United States also indicated higher emissions for some kilns where hazardous wastes were fired.

In both the United States and German studies, a positive correlation was identified between PCDD emission concentration and electrostatic precipitator/stack temperature. In the United States tests, at one facility the electrostatic precipitator temperature recorded was between 255°C and 400°C. The PCDD emissions were highest at 400°C, and decreased fiftyfold at 255°C. This behaviour was observed generally across the set of facilities tested. At temperatures lower than 250°C at the electrostatic precipitator/stack inlet there was no correlation between temperature and PCDD emissions. This is consistent with known mechanisms of PCDD formation within municipal waste incinerator systems (Karstensen 2006b).

More detailed investigations have suggested that – provided combustion is good – the main controlling factor for the level of chemicals listed in Annex C in stack gas is the operating temperature of the dust collection device in the gas cleaning system. Plants equipped with electrostatic precipitators operating at lower temperatures (200°C or less) appear to have low emission concentrations whether or not they use waste (UNEP 2003).

The possible effect of feeding different wastes to the lower-temperature preheater/precalciner was investigated by Lafarge and results are presented in Table 2. Wastes injected at mid or feed-end locations do not experience the same elevated temperatures and long residence times as wastes introduced at the hot end. The observed concentration level of PCDD/PCDF was low in all measurements (Karstensen 2006b).

Table 2. Feeding of wastes to the preheater/precalciner and influence on PCDD/PCDF emissions

Plant	Year	Type of alternative fuel	PCDD/PCDF emissions in ng I-TEQ/Nm ³
1	2002	Animal meal, plastics and textiles	0.0025
2	2002	Animal meal and impregnated sawdust	0.0033
3	2002	Coal, plastic and tires	0.0021 & 0.0041
4	2002	Tires	0.002 & 0.006
5	2002	Petcoke, plastic and waste oil	0.001
6	2002	Petcoke, sunflower shells and waste oil	0.012
7	2002	Tire chips	0.004 & 0.021
8	2002	Solvents	0.07
9	2002	Impregnated saw dust and solvents	0.00003 & 0.00145
10	2002	Solvents	0.00029 & 0.00057
11	2002	Sludge	<0.011
12	2002	Car waste and sludge	0.0036 & 0.07 & 0.0032

The reported data indicate that cement kilns can comply with an emission level of 0.1 ng I-TEQ/Nm³, which is the limit value in several Western European countries' legislation on hazardous waste incineration plants.

5.3.3 Study on releases of PCDD/PCDF through solids

Since the data for stack emissions from cement kilns indicate that well-designed, well-operated facilities can achieve very low exhaust gas concentrations of PCDD/PCDF, it can also be expected that such facilities will have low levels in cement kiln dust recovered from the air pollution control system. The same factors that contribute to low levels remaining in the exhaust to atmosphere argue for low concentrations in the collected solid material. The two main solid materials produced in cement production are cement clinker from the cooler and dust materials trapped in the air pollution control devices.

New analyses of solid materials have been gathered from cement companies participating in the Cement Sustainability Initiative (CSI) (Karstensen 2006b). Eight CSI

companies reported the PCDD/PCDF concentration in cement clinker dust in 2005. Ninety samples showed an average value of 6.7 ng I-TEQ/kg, seemingly strongly influenced by a few high-level samples. The highest concentration reported was 96 ng I-TEQ/kg.

Eight CSI companies reported the PCDD/PCDF concentration in 57 clinker samples in 2005. The average value of all samples was 1.24 ng I-TEQ/kg. The clinker samples came from wet and dry suspension preheater kilns. The highest concentration reported was 13 ng I-TEQ/kg.

Two CSI companies reported the PCDD/PCDF concentration in 11 kiln feed samples in 2005, consisting of raw meal, pellets, and slurry and raw material components. The average value of these samples was 1.4 ng I-TEQ/kg. The kiln feed samples came from wet and dry suspension preheater kilns. The highest concentration reported was 7.1 ng I-TEQ/kg.

5.4 Releases of PCB and HCB

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 PCB₆ emissions, 40 measurements carried out in 13 kilns in Germany in 2001 revealed a maximum concentration of 0.4 µg PCB /Nm³; in nine of the 40 measurements, no PCB were detected. From Vietnam co-incineration of pesticides has shown emissions of dioxin like PCB of 0.001 ng TEQ/m³ and HCB emissions below the detection limit of 31 ng/m³ (Karstensen 2006b).

6. Best available techniques and best environmental practices

The following paragraphs summarize best available techniques and best environmental practices for cement kilns firing hazardous waste.

6.1 General measures for management

6.1.1 Legal aspects

An appropriate legislative and regulatory framework has to be in place to ensure enforcement and to guarantee a high level of environmental protection.

Furthermore, an established waste management regime that emphasizes the waste management hierarchy illustrated in Section III C (ii) on waste management should be established before or in parallel with the formal designation of cement kilns as sanctioned recipients of hazardous wastes, whether as waste-derived fuels or as wastes for disposal. All relevant authorities need to be involved during the permitting process, and in this regard, among other actions, the cement plant operator should:

- Establish and maintain credibility through open, consistent, responsive and ongoing communication with authorities and the public;

- Provide all necessary information to ensure that authorities are able to evaluate the safety and environmental impacts of the processing of hazardous waste;
- Establish community advisory panels early in the planning process;
- The Holcim and the CSI guidelines represent good guidance on BEP in relation to the section.

6.1.2 Environmental aspects

Co- incineration of hazardous wastes should only be performed if the cement kiln operates according to the best available techniques described in these guidelines. If certain provisions for waste quality and waste feeding are met the co-processing of waste will not change the emissions from a cement kiln stack significantly. However, some fuels may contain metals with a high volatility, such as mercury, which has a poor trapping coefficient. To control mercury emissions, it can therefore be necessary to limit mercury inputs into the kiln system. Alternative fuels have to undergo a rigorous acceptance and inspection procedure before being used.

Emission monitoring is obligatory in order to demonstrate compliance with existing laws, regulations and agreements.

6.1.3 Operational aspects

Operators need to ensure that only hazardous waste originating from trustworthy parties will be accepted, considering the integrity of all participants throughout the supply chain. The traceability of the wastes needs to be ensured prior to reception by the facility, with deliveries of unsuitable wastes refused.

Materials transport, handling and storage must be effectively monitored, and full compliance with existing regulatory requirements must be assured. This includes analysis and reporting of parameters such as the heating value, water content, heavy metal content, ash content, sulphur content and chlorine content. Also retained samples should be stored for a certain period of time.

6.1.4 Health and safety aspects

The suitability of the production site must be assessed to avoid risks associated with location (proximity to human habitation, potential impact of releases, logistics, transport) and infrastructure (potential releases of vapours and odours or possibility of leaks that might release hazardous waste or other substances of concern into environmental media, requiring control through application of technical solutions).

Adequate documentation and information on safe waste-derived fuel 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. It is essential that employees, regulatory authorities and local emergency response officials (e.g. fire departments) have such information well before firing of wastes, including hazardous waste, begins in a cement kiln facility.

6.1.5 Communication issues and social responsibility

In the interest of openness and transparency, the cement kiln operator planning to handle and co-incinerate waste, including hazardous or waste-derived fuel, must provide all necessary information to allow stakeholders to understand the purpose of the use of hazardous waste 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, the functions of the parties involved and decision-making procedures. In summary, the following general management aspects should be taken into account:

- General infrastructure, paving, ventilation;
- Good site and facility housekeeping;
- General control and monitoring of basic performance parameters;
- Control and abatement of air emissions (NO_x, SO₂, particles, metals);
- Development of environmental monitoring (establishing standard monitoring protocols);
- Development of audit and reporting systems;
- Implementation of specific permit and audit systems for use of wastes and alternative fuels;
- Demonstration by emission monitoring that a facility can achieve a given emission limit value;
- Occupational health and safety provisions: Cement kilns fired with wastes and alternative fuels need to have appropriate practices to protect workers handling those materials during the feeding process;
- Sufficient qualification and training of staff.

6.2 Specific measures

For new plants and major upgrades, best available techniques for the production of cement clinker are considered to be a dry process kiln with multistage preheating and precalcination. For existing installations, varying degrees of reconstruction may be needed.⁶

6.2.1 Primary measures and process optimization

6.2.1.1 Process optimization

- Ensure rapid cooling of exhaust gases to a temperature lower than 200°C.
- Characterize the parameters that correspond to good operation and use these as a basis to improve other operational performance. Having characterized good kiln operating parameters, establish reference data by adding controlled doses of waste, and assess what are the changes and required controls and practices to control emissions;

- Manage the kiln process to achieve and maintain stable operating conditions, i.e. by optimizing process control (including implementing computer-based automatic control systems) and using modern, gravimetric solid fuel feed systems;
- Minimize fuel energy use by employing preheating and precalcination to the extent possible considering the existing kiln system configuration; and use of modern clinker coolers, enabling maximum heat recovery from the exhaust gas.

Control of chemicals listed in Annex C: Indirect measures for control of chemicals listed in Annex C are an important element of an integrated emission control strategy. Such measures are generally applicable and are relatively simple to implement technically.

6.2.1.2 Hazardous waste preparation

Pretreatment of waste, including hazardous waste, for the purpose of providing a more homogeneous feed and thus more stable combustion conditions may, depending on the nature of the waste-derived fuel, involve drying, shredding, mixing or grinding (see also section 3.4). It is important to give close scrutiny to:

- Good maintenance, housekeeping and procedures appropriate to the safe acceptance, handling and storage of wastes as they arrive at the site, and appropriately designed interim storage facilities taking into account the hazards and characteristics of each waste;
- Good maintenance, housekeeping and operating procedures and appropriately designed storage facilities for the alternative fuel.

These measures are not necessarily specific for control of chemicals to be eliminated and reduced by Annex C, but are essential elements of an integrated emission control strategy.

6.2.1.3 Input controls

- Consistent long-term supply of a given waste or alternative fuel (e.g. a supply of a month or more) is required in order to maintain stable conditions during operation;
- Substances entering the kiln should be carefully selected and controlled; specifications should be set based on product/process or emission considerations and monitored;
- Continuous supply of alternative fuels with specification of heavy metals, chlorine, sulphur;
- Waste-derived fuel should never be used during start-up and shutdown.
- The feeding of raw mix containing waste with organic compounds that could act as precursor should be avoided;
- Halogenated waste should be fed through the main burner.

- In general, waste should be fed through either the main burner or the secondary burner for preheater/precalciner kilns. For the secondary burner it should be ensured that the combustion zone temperature is maintained $>850^{\circ}\text{C}$ for a sufficient residence time (2 s);
- Waste feed containing organic compounds that could act as precursor should not be fed as part of the raw mix;
- Waste-derived fuel should never be used during start-up and shutdown.

Control of chemicals listed in Annex C: Indirect measures for control of such chemicals are an important element of an integrated emission control strategy. Such measures are generally applicable and are generally simple to implement technically.

6.2.1.4 Stabilization of process parameters

It is important for combustion and process stability to ensure:

- Consistency in fuel characteristics (both alternative and fossil);
- Consistency in fuel supply rate or frequency of introduction of batch-charged materials;
- That adequate excess oxygen is supplied to achieve good combustion;
- That concentrations of CO in exhaust gases are monitored and do not exceed pre-established levels reflecting poor combustion conditions.

Control of chemicals listed in Annex C: Indirect measures for control of such chemicals are an important element of an integrated emission control strategy. Such measures are generally applicable and help ensure stable operating conditions.

6.2.1.5 Process modification

The off-gas dust (also known as cement kiln dust) must be managed carefully. In many cases it may be fed back into the kiln to the extent that it can be demonstrated to be practicable and to avoid excessive emissions of volatile metals and alkali salts. Where this recycle stream can be maximized it will reduce issues related to disposal of the dust. Dust that cannot be recycled must be managed in a manner demonstrated to be safe. Depending upon the level of contaminants of concern (e.g. heavy metals, persistent organic pollutants), this material can in some cases be considered hazardous waste and may then require the special handling and disposal measures mandated by such a determination.

Control of chemicals listed in Annex C: Indirect measures for control of such chemicals are an important element of an integrated emission control strategy.

6.2.1.6 Summary of primary measures

In general, the primary measures mentioned above are sufficient to achieve an emission level below $0.1 \text{ ng I-TEQ/Nm}^3$ in flue gases for new and existing installations. Where all

of these options do not lead to performance down to 0.1 ng I-TEQ/Nm³, secondary measures may be considered, as described below.

6.2.2 Secondary measures

The secondary measures cited below are usually installed for the purpose of controlling pollutants, other than unintentionally formed persistent organic pollutants, but they may also lead to a simultaneous reduction in emissions of chemicals listed in Annex C.

6.2.2.1 Further improvement of dust abatement and recirculation of dust

These measures will not reduce levels of chemicals listed in Annex C present in the gas phase in the exhaust to any appreciable extent. As a result, the effectiveness of this strategy will generally decrease with increasing temperature of the particulate collection system. Changing from no recirculation of cement kiln dust to full recirculation will change its chemical composition over time, increasing the alkali content and leading to operating issues; a certain fraction of the collected dust must be disposed of and where high recirculation rates are practiced the dust is likely to be enriched in semi-volatile and volatile heavy metals, mandating careful handling procedures and safe disposal at a facility designed to treat or contain hazardous wastes. General applicability; moderate technical construction requirements; good capture of the fraction of chemicals listed in Annex C which are bound to particles.

Rotary kilns are generally equipped with electrostatic precipitators, on account of the relatively high exhaust gas temperatures. Fabric filters are also used, particularly on preheater kilns, where exhaust gas temperatures are lower.

Shaft kilns are usually fitted with fabric filters. Wet scrubbers are sometimes used. Lime grinding plants use fabric filters to collect the product and dedust the conveying air. Hydrating plants, with exhaust gases saturated with water vapor at about 90°C, are generally fitted with wet scrubbers, although fabric filters are increasingly being used where the feed lime has a high reactivity.

Information from the European Union (European Commission 2001) indicates that particulate matter from point sources can be effectively removed by application of:

- Electrostatic precipitators with fast measuring and control equipment to minimize the number of CO trips;
- Fabric filters with multiple compartments and burst bag detectors.

The emission level associated with these best available techniques is 20–30 mg dust/m³ on a daily average basis. This emission level can be achieved by electrostatic precipitators or fabric filters at the various types of installations in the cement industry.

6.2.2.2 Activated carbon injection

Where fabric filters are used for particulate control purposes, it is possible to inject powdered activated carbon upstream of the fabric filter and achieve very good removal of metals and organic compounds. Pollutants are collected by adsorption on the surface

of the carbon both as it is dispersed in the exhaust stream, and as the exhaust passes through the filter cake formed on the inside of the fabric filter bags. A low operating temperature is critical to successful application of this technique, since at temperatures within the range for de novo synthesis (250°–400° C) activated carbon could serve as a carbon source for PCDD/PCDF formation. Activated carbon also performs better at adsorbing metals and PCDD/PCDF at temperatures below 200° C. At the same time, the temperature must be maintained above the dew point for the exhaust gases in order to avoid condensation and blinding of the bags. An operating temperature in the vicinity of 160° C is generally used, although with careful monitoring somewhat lower values may be achieved. Temperature control is usually achieved by evaporative cooling and carbon is typically injected in or just downstream of the evaporative cooler. It should be noted that if cement kiln dust is to be recycled to the kiln this technique may not be highly effective for mercury emission control, as collected mercury will be re-released in the kiln and the cement kiln dust bleed stream for disposal may need to be a large fraction of the total in order to achieve positive control.

This technique has general applicability for control of Annex C chemicals, with very good (>90%) capture expected when operating temperatures are optimized properly; it has low to moderate technical construction requirements and is better suited to retrofit situations than the following two options.

6.2.2.3 Activated carbon filter

This measure has high removal efficiency for certain pollutants (>90% generally; >99% for some compounds). Pollutants such as sulphur dioxide (SO₂), organic compounds, metals, ammonia (NH₃), ammonium (NH₄⁺) compounds, hydrogen chloride (HCl), hydrogen fluoride (HF) and residual dust (after an electrostatic precipitator or fabric filter) may be removed from exhaust gases that have been treated in an activated carbon bed. The only activated carbon filter installed at a cement works in Europe is that at Siggenthal, Switzerland. The Siggenthal kiln is a four-stage cyclone preheater kiln with a capacity of 2,000 tons of clinker per day. Measurements show high removal efficiencies for SO₂, metals and PCDD/PCDF (European Commission 2001).

Control of chemicals listed in Annex C: General applicability; demanding technical construction.

6.2.2.4 Selective catalytic reduction

In general, selective catalytic reduction installations are applied for NO_x control. The process reduces NO and NO₂ to N₂ using NH₃ as a reducing agent in the presence of an appropriate catalyst at a temperature range of about 300°C – 400°C, which would require heating of the exhaust gases from a typical cement kiln. Only a subset of the catalysts capable of reducing nitrogen oxides are also suited to the destruction of Annex C pollutants such as PCDD/PCDF. To date, selective catalytic reduction for NO_x control has only been tested on preheater and semi-dry (Lepol) kiln systems, but it may be applicable to other kiln systems as well (European Commission 2001). Its relatively high capital cost, along with significant energy costs for reheat of the exhaust gases in order to use it, make this solution appear unlikely to be economically favorable in general

application. The first full-scale plant (Solnhofer Zementwerke) has been in operation since the end of 1999 (PTS 2004).

Control of chemicals listed in Annex C: Demanding technical construction and capital/operating costs; expected excellent control of chemicals listed in Annex C by appropriately selected catalysts.

6.2.2.5 Activated carbon injection, an emerging technology

It is possible to inject powdered activated carbon upstream of the dust collecting filter, which may achieve efficient removal of metals and organic compounds. However, the following remarks should be made:

- A low operating temperature to $<160^{\circ}\text{C}$ is critical to successful application of this technique;
- At the same time, the temperature must be maintained above the acid dew point to avoid condensation or corrosion;
- If cement kiln dust is to be recycled to the kiln, which is usually the case, this technique will not be effective for mercury emission control, as collected mercury will once again be re-released in the kiln;
- This carbon injection technology has not been demonstrated for the control of PCDD/PCDF emission from cement kilns and has only been applied in municipal waste incinerators.

7. Performance requirements based on best available techniques

Performance requirements based on best available techniques for control of PCDD/PCDF in flue gases should be $<0.1 \text{ ng I-TEQ/Nm}^3$ with reference conditions of 273 K, 101.3 kPa, 11% O_2 and a dry gas basis.

8. Monitoring of pollutant emissions and operation parameters

To control kiln process, continuous measurement is recommended for the following parameters (European Commission 2001):

- Pressure;
- Temperature;
- O_2 content;
- NO_x ;
- CO , and possibly when the SO_x concentration is high;

- SO₂ (a technique is being developed to optimize CO with NO_x and SO₂).

Above these parameters control of mercury (if mercury content in the waste is high) should be ensured.

To accurately quantify the emissions, continuous measurement is best available technique for the following parameters (these may need to be measured again if their levels can change after the point where they are measured to be used for control):

- Exhaust volume (can be calculated but the process is regarded by some as complicated);
- Humidity;
- Temperature at particulate matter control device inlet;
- Dust/particulate matter;
- O₂;
- NO_x;
- Dust;
- SO₂;
- CO.

Regular periodical monitoring is best available technique for the following substances:

- Metals and their compounds;
- Total organic carbon/organic components;
- HCl, HF;
- NH₃;
- PCDD/PCDF.

Measurements of the following may be required occasionally under special operating conditions:

- Destruction and removal efficiency, in the case of destruction of persistent organic pollutants in cement kilns;
- Benzene, toluene, xylene;
- Polycyclic aromatic hydrocarbons;
- Other organic pollutants (principal organic hazardous constituents, e.g. chlorobenzenes, PCB including coplanar congeners, chloronaphthalenes).

It is especially important to measure metals when wastes with higher metal content are used as raw materials or fuels.

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- ² This Reference Document is currently (2006) under revision.
- ³ CEMBUREAU contribution to Cement & Lime BREF Revision Energy Efficiency; 15 May 2006
- ⁴ Communication by IPEN
- ⁵ 1 ng (nanogram) = 1×10^{-12} kilogram (1×10^{-9} gram); Nm³ = normal cubic metre, dry gas volume measured at 0°C and 101.3 kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.
- ⁶ The dry process is only appropriate in the case of limestone as a raw material feed. It is possible to utilize preheater/precalciner technology to process chalk, with the chalk slurry dried in a flash dryer at the front end of the process.

