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Development of guidelines on best available techniques and provisional guidance on best environmental practices relevant to the provisions of Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants

DRAFT GUIDELINES ON BAT AND BEP FOR
FOR CEMENT KILNS FIRING HAZARDOUS WASTES

Note by the Secretariat

The attached was submitted by Ms. Steffi Richter (Germany) who coordinated its development. This note and the attached have not been formally edited.

[1] UNEP/POPS/EGB.2/1.

Draft Guidelines on BAT and BEP

for Cement kilns firing hazardous waste

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1. Introduction

Global production of cement is estimated at 1,660 million tonnes per year,[i] a large part of which is based on wet processes.[ii] Cement production in Europe amounts to 190 million tonnes per year,[iii] more than 75% of which is based on dry processes due to the availability of dry raw materials,[iv] 16 % is based on semi-dry or semi-wet processes and 6% in wet processes.[v]

The typical capacity of a new European kiln is 3,000 tonnes of clinker per day. [vi] In the US, about 75% of cement is also produced by dry process kilns that have capacities of about 400,000 tonnes per year.[vii]

2. Cement Production Processes

The basic chemistry of the cement manufacturing process begins with the decomposition of calcium carbonate (CaCO3) at about 900 °C to leave calcium oxide (CaO, lime) and liberate gaseous carbon dioxide (CO2); this process is known as calcination. This is followed by the clinkering process in which the calcium oxide reacts at high temperature (typically 1400-1500 °C) with silica, alumina, and ferrous oxide to form the silicates, aluminates, and ferrites of calcium which comprise the clinker. The clinker is then ground or milled together with gypsum and other additives to produce cement.

2.1. In the Rotary Kiln

The raw feed material (*Raw meal*) 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 “counter-current” 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, 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, uncombustible material.

2.2. After the Rotary kiln

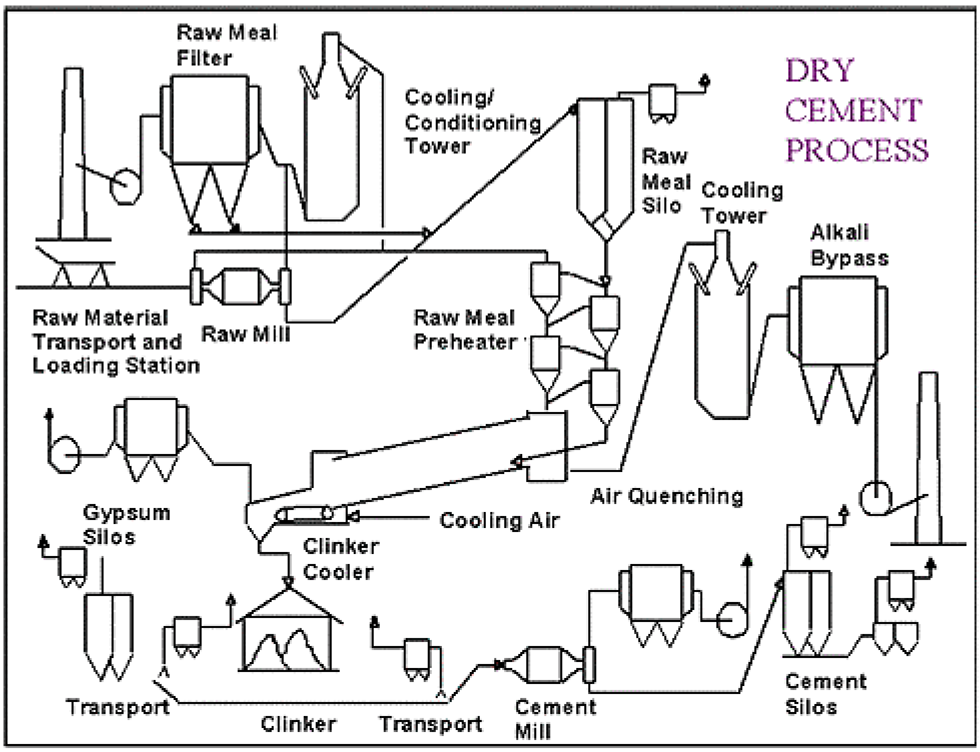
The clinker leaves the hot end of the kiln, at a temperature of about 1,000 ^{o}C. It falls into a *clinker cooler*, typically a moving grate through which cooling air is blown. The clinker is blended with gypsum and ground in a ball mill to produce the final product, cement.

The cement is pneumatically conveyed from the finish *cement mill* to large, vertical storage silos in the packhouse or shipping department. Cement is withdrawn from the *cement storage silos* by a variety of feeding devices and conveyed to loading stations in the plant or directly to transport vehicles.

2.3. Production Process in general

Each of the five different processes used for the pyroprocessing step of cement production accomplishes the required physical/chemical steps. However, the five processes vary with respect to equipment design, method of operation, and fuel consumption.

Figure: Rotary kiln with cyclone preheater and waste gas dust collection



The main process routes for the manufacture of cement used for the pyroprocessing step of cement production accomplishes the required physical/chemical steps. They vary with respect to equipment design, method of operation, and fuel consumption.

- 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.
  - **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 counter-current 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 that of the conventional long dry kilns, the length of the preheater kiln is shorter. With preheater systems, it is often 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.

- **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. 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, since 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 also requires 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.

- In the **semi-dry process** dry raw meal is pelletised with 12 % to 14 % water and fed into a grate preheater before the kiln or to a long kiln equipped with crosses, on which they are dried and partially calcined by hot kiln exhaust gases before being fed to the rotary kiln.
- In the **semi-wet process** the slurry is first dewatered in filter presses. The filter cake is extruded into pellets and fed either to a grate preheater or directly to a filter cake drier for raw meal production.
- 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 drier. The wet process is an older process with lower emissions of kiln dust at one hand, but higher energy demands because of water evaporation from the slurry.

2.4 Fuels

Various fuels can be used to provide the heat required for the process. Three different types of fuels are mainly used in cement kiln firing; in decreasing order of importance these are:

- pulverised coal and petcoke;
- (heavy) fuel oil;

- natural gas.

2.4.1. Use of waste as fuel

In the case of wastes, that are fed through the main burner, will be decomposed in the primary burning zone, at temperatures up to 2000^{o}C. Waste fed to a secondary burner, preheater or precalciner is not adequate, as it will be burnt at lower temperatures, which not always is enough to decompose halogenated organic substances. Volatile components in material that is fed at the upper end of the kiln or as lump fuel can evaporate. These components do not pass the primary burning zone and may not be decomposed or bound in the cement clinker. Therefore the use of waste containing volatile metals (mercury, thallium) or volatile organic compounds can result in an increase of the emissions of mercury, thallium or VOCs when improperly used. Types of waste frequently used as fuels in cement kilns are:

- Used tyres
- Waste oils
- Sewage sludge
- Rubber
- Waste woods
- Plastics
- Paper waste
- Paper sludge
- Spent solvents

Preparation of different types of waste for use as fuel is usually performed outside the cement plant by the supplier or by waste-treatment specialists organisations. This means they only 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/preparation plants to be multi-purpose.

3. Process Outputs

3.1. General Inputs and Outputs

The main environmental issues associated with cement production are emissions to air and energy use. Waste water discharge is usually limited to surface run off and cooling water only and causes no substantial contribution to water pollution.

Primary process outputs of cement production are

- Product: clinker, when grounded cement;
- Kiln exhaust gas: Typical kiln exhaust gas volumes expressed as m^3/Mg of clinker (dry gas, 101.3 kPa, 273 K) are between 1700 and 2500 for all types of kilns. Suspension preheater and precalciner kiln systems normally

have exhaust gas volumes around 2000 m^3/Mg of clinker (dry gas, 101.3 kPa, 273 K).

Mass balance for the production of 1 kg cement[viii]

10 % excess air
Raw meal factor: 1.54
Clinker factor: 0.75
Specific energy: 3.35 MJ/kg Clinker
Air: 10 - 11 Vol . % O2

Fuel: heavy fuel oil
Calorific value: 40000 kJ/kg (on a dry basis)

Input:

1150 g raw material
63 g fuel
984 g air
+ raw material moisture

1050 g air

↓

Burning process (Dry process)

↓

Emissions :

	CO_2	600 g (404 g CO2 from raw material, 196 g CO2 from burning)
	N_2	1566 g
	O_2	262 g
	H_2O	69 g + raw material moisture

Output:

750 g clinker **+**

+ { **250 g**
gypsum
filler
blast furnace slag **+ air**
fly ash

Grinding

↓

Sum: 1000 g Cement

- Cement kiln dust (CKD): In the U.S., some 64% of CKD is recycled back into the kiln and the remainder, which is generated at the rate of about 40 kg/ton of clinker, [ix] is primarily buried in landfills.[x] Holcim, one of the world's largest cement producers, sold or landfilled 29 kg CKD per tonne clinker in 2001.[xi] Recycling CKD directly to the kiln generally results in a gradual increase in alkali content of generated dust that may damage cement kiln linings, produce inferior cement, and increase particle emissions.[xii] In Europe, CKD is commonly added directly to the product cement.[xiii]

- Alkali bypass exhaust gas: At facilities equipped with an alkali bypass, the alkali bypass gases are released from a separate exhaust stack in some cases and from the main kiln stack at others. According to the U.S. Environmental Protection Agency, the pollutants in this gas stream are similar to those in the main kiln exhaust gases so that similar pollution abatement equipment and monitoring is required.[xiv] An alkali bypass ratio of more than 10% is commonly required for alkali removal.[xv] However, a bypass ratio of 30% has also been reported. [xvi]

- Alkali bypass exhaust gas dust: Depending on the type of air pollution control used for alkali bypass gases, the collected dust can be expected to be similar in content to CKD.

Kiln systems with 5 cyclone preheater stages and precalciner are considered standard technology for ordinary new plants, such a configuration will use 2900-3200 MJ/Mg clinker. To optimise the input of energy in other kiln systems it is possible to change the configuration of the kiln to a short dry process kiln with multi stage preheating and precalcination. This is usually not feasible unless done as part of a major upgrade with an increase in production. The application of the latest generation of clinker coolers and recovering waste heat as far as possible, utilising it for drying and preheating processes, are examples of methods which cut primary energy consumption.

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

Energy use will be increased by most type of end-of-pipe abatement. Some of the reduction techniques described below will also have a positive effect on energy use, for example process control optimisation.

This guidance addresses cement kilns co-firing hazardous waste, municipal waste, medical waste, sewage sludge, and other wastes, such as used tires, waste oil, plastic waste, etc. Only specific waste flows meet the demands made by these processes: the calorific value must be high enough and the ashes should not contain high concentrations of contaminations. Furthermore, the waste should not contain high levels of volatile chemicals[xvii].

3.2 Emissions of PCDD/F

Any chlorine input in the presence of organic material may potentially cause the formation of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in heat (combustion) processes. PCDDs and PCDFs can be formed in/after the preheater and in the air pollution control device if chlorine and hydrocarbon precursors from the raw materials are available in sufficient quantities. It is important that as the gases are leaving the kiln system they should be cooled rapidly through this range. In practice this is what occurs in preheater systems as the incoming raw materials are preheated by the kiln gases. Due to the long residence time in the kiln and the high temperatures, emissions of PCDDs and PCDFs is generally low during steady kiln conditions. In this case,cement production is rarely a significant source of PCDD/F emissions. Nevertheless, from the data reported in the document "Identification of Relevant Industrial Sources of Dioxins and Furans in Europe" there would still seem to be considerable uncertainty about dioxin emissions.[xviii]

The reported data indicate that cement kilns can mostly comply with an emission concentration of 0.1 ng TEQ/Nm^3, which is the limit value in several Western European legislation for hazardous waste incineration plants. German measurements at 16 cement clinker kilns (suspension preheater kilns and Lepol kilns) during the last 10 years indicate that the average concentration amounts to about 0.02 ng TE/m^3. [xix]

4. Best Available Techniques (BAT) and Best Environmental Practices (BEP) for cement kilns

4.1. General measures for management

(1) General infrastructure, paving, ventilation.

(2) General control and monitoring of basic performance parameters.

(3) Control and abatement of gross air emissions (gases NOx, SO2, particles, metals).

(4) Development of environmental monitoring (establishing standard monitoring protocols).

(5) Development of audit and reporting systems.

(6) Implementation of specific permit and audit systems for waste burning.

(7) Demonstration by emission monitoring that a new facility can achieve a given emission limit value.

4.2 Specific measures

Management options	Release characterization	Applicability	Other considerations
In reviewing technology the dry process technology is preferred as BAT in major retrofit or new processes. (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 drier at the front end of the process)	Indirect measure, minor effective for UPOPs reduction in specific but elements of an integrated concept	Partially considerable reconstruction needed	BAT measures for clinker production
Characterize a good operation and use this as a basis to improve other operational performance.	Indirect measure, minor effective for UPOPs reduction in specific but elements of an integrated concept	general applicable, **simple** technical construction	
Having characterized a good kiln, establish reference data by adding controlled doses of waste and look at changes and required controls and practice to control emissions.	Indirect measure, minor effective for UPOPs reduction in specific but elements of an integrated concept	general applicable, **simple** technical construction	
Cement kilns feeding waste need to have provision of practices to protect workers on the handling of those materials (not issue once fed).	Not specific for UPOPs, but elements of an integrated concept		
The off gas dust should be put back to the kilns to the maximum where practicable to reduce the disposal issues and related possible emissions. Dust, that can not be recycled, should be managed in a manner to be demonstrated to be safe.	Indirect measures, minor effective for UPOPs reduction in specific but elements of an integrated concept	general applicable, **simple** technical construction	

Recognizing the need to distinct difference in how it is applied when feeding waste as opposed to non hazardous waste.	Not specific for UPOPs, but elements of an integrated concept		
Waste should not be fed to the secondary burners or preheaters.		general applicable, **simple** technical construction	
Consistent long term supply of secondary feeds and waste (supplies of a month or more) is required to maintain stable conditions in the operation.		general applicable, **simple** technical construction	
a) Primary measures and process optimization to reduce PCDD/PCDF			
General primary measures for the manufacturing of cement for reducing environmental impacts [xx] Management of the kiln process to achieve stable operating conditions, which may be achieved by applying: - process control optimization, including computer-based automatic control systems; - the use of modern, gravimetric solid fuel feed systems. Minimizing fuel energy use by means of: - preheating and precalcination as far as possible, considering the existing kiln system configuration; - the use of modern clinker coolers enabling maximum heat recovery; - heat recovery from waste gas. Minimizing electrical energy use by means of: - power management systems; - grinding equipment and other electricity based equipment with high energy efficiency. Careful selection and control of substances entering the kiln, to minimize introduction of sulfur, nitrogen, chlorine, metals and volatile organic compounds.			
o Continuous supply of fuel and waste with			
- specification of ▪ Heavy metals, ▪ Chlorine (limitation, product/ pro-	Indirect measures, minor effective for UPOPs reduction	general applicable, **simple** technical construction	

cess dependent), ▪ Sulfur.	in specificbut elements of an integrated concept		
- Input controls.			
o Pre-treatment of waste (waste specific) with the objective to provide a more homogeneous feed and more stabile combustion conditions: - Drying - Shreddering - Mixing - Grinding	Indirect measures, minor effective for UPOPs reduction in specificbut elements of an integrated concept	general applicable, **simple** technical construction	
o Well maintained and appropriate storage of fuel	Not specific for UPOPs, but elements of an integrated concept		
o Well maintained and appropriate storage and handling of wastes and sites	Not specific for UPOPs, but elements of an integrated concept		
o Feeding of waste through the main burner or the secondary burner at precalciner/pre-heater kilns [temperature > 900°C]		general applicable, **simple** technical construction	Contaminated waste should fed to the primary burner only, as usually in the precalciner/pre-heater temperatures are below 900°C (deacidification of raw material is performed at 850°C)
o No waste feed as part of raw-mix if it includes organics	Indirect measures, minor effective for UPOPs reduction in specificbut elements of an integrated concept	general applicable, **simple** technical construction	UPOP-formation is possible in relevant temperature ranges

o Stabilisation of process parameters - Regularity in fuel characteristics (both alternative and fossil) - Regular dosage - Excess oxygen - Monitoring of CO	Indirect measures, minor effective for UPOPs reduction in specificbut elements of an integrated concept	general applicable,	Is to be ensured to stabilize operating conditions,
o No waste feed during start-up and shut down	Indirect measures, minor effective for UPOPs reduction in specific but elements of an integrated concept	general applicable, **simple** technical construction	
o Quick cooling of kiln exhaust gases lower than 200°C	Indirect measures, minor effective for UPOPs reduction in specificbut elements of an integrated concept		The critical range of temperature is usually passed through quickly in the clinker process. Efficiency of this measure could be low with high technical demand if existing plants are equipped afterwards.
Primary measures have shown to be sufficient to reach in existing installations 0.1 ng/m³ for existing and new sources. Monitoring should be done. If all of these options do not lead to a performance lower than 0.1 ng/m³ secondary measures may be considered such as			
b) Secondary measures:			
o Activated carbon filter	High efficiency > 90 %	general applicable, **demanding** technical construction	
o Selective catalytic reduction (SCR)	High efficiency	General applica-	Improvement of UPOP-control

		ble, **demanding** technical construction	by efficient catalysts
o Further improvement of dust abatement and recirculation of dust	Efficiency may decrease with decreasing temperature of dust precipitation	general applicable, **medium** technical construction	Captures UPOPs bound by particles

5. Performance requirements based on BAT for new and existing cement kilns

Performance Requirement based on BAT for new and existing cement kilns for PCDD/F should be < 0,1 ng TEQ/m^3

6. Monitoring

To control kiln process, continuous measurements are recommended for the following parameters:

- pressure,
- temperature,
- O_2-content
- NO_x,
- CO, and possibly when the SOx concentration is high
- SO_2 (it is a developing technique to optimise CO with NOx and SO2)

To accurately quantify the emissions, continuous measurements are recommended 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 is regarded by some to be complicated),
- humidity (can be calculated but is regarded by some to be complicated),
- temperature,
- dust,
- O_2,
- NO_x,
- SO_2, and
- CO

Regular periodical monitoring is appropriate to carry out for the following substances:

- metals and their compounds,
- TOC,
- HCl,
- HF,
- NH_3, and

- PCDD/Fs

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

- BTX (benzene, toluene, xylene),
- PAH (polyaromatic hydrocarbons), and
- other organic pollutants (for example chlorobenzenes, PCB (polychlorinated biphenyls)

including coplanar congeners, chloronaphthalenes, etc.).

It is especially important to measure metals when wastes with enhanced metals contents are used as raw materials or fuels.

7. References

i de Bas, P., 2002. The economics of measurement of emissions into the air. Pembroke College, Oxford, UK: European Measurement Project.

ii DFIU/IFARE, 2002. Cement/Line industry: Draft Background Document in preparation of the 5th EGTEI panel meeting, 29 November 2002. www.citepa.org/forums/egtei/cement_lime_draft.pdf

iii de Bas, P., 2002. The economics of measurement of emissions into the air. Pembroke College, Oxford, UK: European Measurement Project.

iv DFIU/IFARE, 2002. Cement/Line industry: Draft Background Document in preparation of the 5th EGTEI panel meeting, 29 November 2002. www.citepa.org/forums/egtei/cement_lime_draft.pdf

v Wulf-Schnabel, J., Lohse, J., 1999. Economic evalution of dust abatement in the European Cement Industry. A report prepared for the European Commission DG XI, Contract No. B4-3040/98/000725/MAR/E1. http://www.oekopol.de/en/Archiv/archiv.htm

vi Wulf-Schnabel, J., Lohse, J., 1999. Economic evalution of dust abatement in the European Cement Industry. A report prepared for the European Commission DG XI, Contract No. B4-3040/98/000725/MAR/E1.

vii Portland Cement Association, Industry Overview. http://www.portcement.org/cem/cementindustry_industryover2.asp viii Integrated Pollution Prevention and Control (IPPC) – Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industry, EIPPCB December 2001 http://eippcb.jrc.es/pages/FActivities.htm

ix WISE, 2002. Waste Generation: Indicator: Volume of Cement Kiln Dust Produced and Reused. http://www.pepps.fsu.edu/WISE/

x U.S. Environmental Protection Agency, Draft Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-*p*-Dioxin (TCDD) and Related Compounds, Part I: Estimating Exposure to Dioxin-Like Compounds, Chapter 5: Combustion Sources of CDD/CDF: Other High Temperature Sources, EPA/600/P-00/001Bb, Washington, D.C., September 2000

xi Holcim, Environmental Performance, p. 17. www.holcim.com

xii U.S. Environmental Protection Agency, 1998. Technical Background Document on Ground Water Controls at CKD Landfills. Draft. Washington, D.C.: Office of Solid Waste, U.S. Environmental Protection Agency.

xiii Lohse, J., Wulf-Schnabel, J., 1996. Expertise on the Environmental Risks Associated with the Co-Incineration of Wastes in the Cement Kiln "Four E" of CBR Usine de Lixhe, Belgium. Hamburg, Germany: Okopol. http://www.oekopol.de/Archiv/Anlagen/CBRBelgien.htm

xiv U.S. Environmental Protection Agency, 1999. National Emission Standards for Hazardous Air Pollutants for Source Categories; Portland Cement Manufacturing Industry; Final Rule. 40 CFR part 63, 14 June 1999.

xv Sutou, K., Harada, H., Ueno, N., 2001. Chlorine bypass system for stable kiln operation and recycling of waste. Technical Conference on Cement Process Engineering 21st plenary session of the VDZ Process Engineering Committee Düsseldorf, Germany(22.02.2001).

xvi Holsiepe, D., Shenk, R., Keefe, B., 2001. Partners in Progress: A Case Study on Upgrading for the New Millenium, Part 1. Cement Americas. http://cementtour.cementamericas.com/ar/cement_partners_progress_case_2/

xvii Bouwmans, I., Hakvoort, R., 1998. A Framework for the Evaluation of the Environmental Merits of Waste Co-Incineration. IECEC-98-1225. 33rd Intersociety Engineering Conference on Energy Conversion, Colorado Springs, CO, August 2-6, 1998.

xviii Landesumweltamt Nordrhein-Westfalen, Commissioned by EC DG XI, LUA-Materialien No. 43, Identification of

Relevant Industrial Sources of Dioxins and Furans in Europe, The European Dioxin Inventory, (1997)

xix Forschungsinstitut der Zementindustrie, Düsseldorf, Germany M. Schneider, K. Kuhlmann, F. Söllenböhmer PCDD/F–Emissions from German Cement Clinker Kilns Organohalogen Compounds, Volume 27, (1996)

xx Marlowe, I., Mansfield, D., 2002. Toward a Sustainable Cement Industry. Substudy 10: Environment, Health & Safety Performance Improvement. AEA Technology. http://www.wbcsdcement.org/.