

Section V.B.

Guidance by source category: Annex C, Part II Source Categories

Cement kilns firing hazardous waste

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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 dry processes.ⁱⁱ Cement production in Europe amounts to 190 million tonnes per year^j, more than 75% of which is based on dry processes due to the availability of dry raw materialsⁱⁱ, 16 % is based on semi-dry or semi-wet processes and 6% in wet processes.ⁱⁱⁱ In China the major part of the cement is produced in vertical shaft kilns which show low energy efficiency and poor environmental performance^{iv}.

The typical capacity of a new European kiln is 3,000 tonnes of clinker per dayⁱⁱⁱ. In the US the average kiln in use today produces 468,000 metric tons per year (in 2002). Currently, about 81% of the cement produced in the United States is manufactured using dry process technology.^v

The cement industry is an energy intensive industry with energy typically accounting for 30-40% of production costs (i.e. excluding capital costs). Traditionally, the primary fuel used is coal. A wide range of other fuels are also used, including petroleum coke, natural gas and oil. In addition to these fuel types, the cement industry uses various types of waste as fuel. In the European cement industry the share of waste in total fuel consumption amounts to ca. 12% (in 2001)^{vi}.

2. Cement Production Processes

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 1400-1500 °C) with silica, alumina, and ferrous oxide to form the silicates, aluminates, and ferrites of calcium which comprise the portland clinker. This clinker is then ground together with gypsum and other additives to produce cement.

2.1. In the rotary kiln

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 "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 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, uncombustible material.

2.2. After the rotary kiln

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. 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 packhouse 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.

2.3. Production process in general

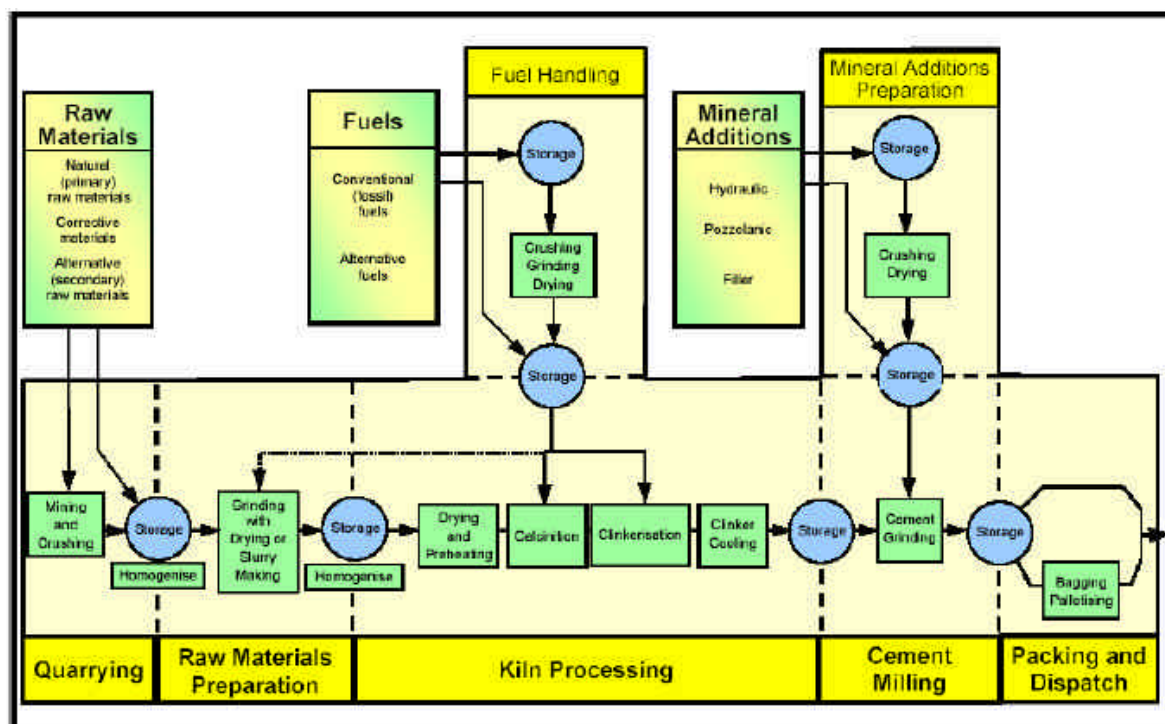


Figure 1: Processes identification and system boundaries of cement production

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^{vi}.

- 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 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.
- **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 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.
- 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.

All 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 are not used at cement kilns since the raw materials are highly alkaline and provide acid gas control ^{viii}.

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.

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

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

2.4.1. Alternative fuel preparation

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.

Types of waste frequently used as fuels in cement kilns include:

- Used tyres
- Waste oils
- Sewage sludge
- Rubber
- Waste wood
- Plastics
- Paper waste
- Paper sludge
- Animal meal
- Spent solvents

For smooth operation and combustion some important criteria have to be considered for conditioning. Production of a homogeneous clinker requires a constant and complete combustion of the fuel. The oxidation of the fuel constituents runs any quicker when the fuels are intimately mixed and the specific surface is larger - that means to assure- especially in the case of liquid fuel where the injection has to be as smooth as possible, vs. solid fuels on intimate mixture with other fuels used at the same time - the biggest possible surface due to perfect conditioning (low particle size).^{vii}

2.4.2. Use of hazardous waste as fuel

Cement kilns utilise wastes commercially (i.e., they accept waste from off-site generators) for use as a fuel supplement 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 at the high temperature section^{viii}.

In the case of hazardous wastes a complete decomposition of toxic compounds such as halogenated organic substances has to be ensured. Wastes that are fed through the main burner will be decomposed in the primary burning zone at temperatures up to 2000 °C. Waste fed to a secondary burner, preheater or precalciner will be burnt at slightly lower temperatures but it is anticipated that the burning zone temperatures in the precalciner will be in the range of 1000°C - 1200°C.

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 may result in an increase of the emissions of mercury, thallium or VOCs when improperly used.

The hazardous waste used as a fuel by the cement industry consists mainly of organic material, but may also contain trace 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 (DRE) for chemicals such as methylene chloride, carbon tetrachloride, trichlorobenzene, trichloroethane and PCBs has typically been measured at 99.995% and better^{viii}.

The potential for using cement kilns to incinerate PCBs has been investigated in many countries. The destruction and removal efficiencies (DRE) determined from several trial burns indicate that cement kilns are effective at destroying PCBs. A

DRE of 99.9999% is required by the US Toxics Substances Control Act for the incineration of these compounds.

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 ground cement;
- Kiln exhaust gas: Typical kiln exhaust gas volumes expressed as m³/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 m³/Mg of clinker (dry gas, 101.3 kPa, 273 K).
- Cement kiln dust (collected in the dust collection equipment, 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.

3.2 *Energy use*

New kiln systems with 5 cyclone preheater stages and precalciner will require on average 2900-3200 MJ/Mg clinker. To optimise 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 multi stage preheating and precalcination. This is usually not feasible unless part of a major upgrade with an increase of production.

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.

3.3 *Emissions of PCDD/PCDF*

Any chlorine input in the presence of organic material may potentially cause the formation of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in heat (combustion) processes. PCDD and PCDF 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. 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 PCDD and PCDF is generally low during steady kiln conditions. In this case, cement production is rarely a significant source of PCDD/PCDF 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.^{xvii}

In the USA, tests have indicated that higher emissions were found for some kilns where hazardous wastes were fired. More detailed investigations suggested that – provided combustion is good - the main controlling factor is the temperature of the dust collection device in the gas cleaning system. The plants equipped with low temperature electrostatic precipitators appear to have well controlled emissions with or without waste fuels^{xviii}.

One positive correlation identified both in the US and German studies was that between dioxin emission concentration and ESP/stack temperature. In the US tests at one facility the ESP temperature recorded between 255°C and 400°C. The dioxin emissions were highest at 400°C, and decreased 50-fold at 255°C. This correlation was generally observed across all facilities tested. At temperatures lower than 250°C in the ESP/stack inlet there is no correlation between temperature and dioxin emissions. This is consistent with known mechanisms of dioxin formation within municipal waste incinerator systems^{viii}.

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

In a recent survey performed by CEMBUREAU 230 PCDD and PCDF measurements from 110 cement kilns and 10 countries were presented. The countries covered by the survey were Czech Republic, Denmark, France, Germany, Hungary, Italy, Norway, Spain, The Netherlands and United Kingdom. The measurements were performed under standard conditions (dry gas, 273 K, 101.3 kPa and 10% O₂) and showed that the average concentration was 0.016 ng I-TEQ/m³ for all measurements. The lowest and highest concentration measured were <0.001 and 0.163 ng I-TEQ/m³ respectively ^{viii}.

The Holcim Cement Company operates cement kilns world-wide. In a recent report from Holcim the average PCDD/PCDF values for 2001 and 2002 are given with 0.041 ng TEQ/Nm³ (71 kilns) and 0.030 ng TEQ/Nm³ (82 kilns) respectively. 120 of these measurements were from OECD countries with an average value of 0.0307 ng TEQ/Nm³; the minimum and maximum value measured was 0.0001 and 0.292 ng TEQ/Nm³ respectively, with 9 long wet kilns being above 0.1 ng TEQ/Nm³. 29 of these measurements were from non-OECD countries with an average value of 0.0146 ng TEQ/Nm³; the minimum and maximum value measured was 0.0002 and 0.074 ng TEQ/Nm³ respectively, with no measurements being above 0.1 ng TEQ/Nm³ ^{viii}.

The Table 1 summarises the results of PCDD/PCDF measurements reviewed in the WBCSD-SINTEF Report on the Formation and Release of POP's in the Cement Industry.

Table 1: Summary of PCDD/PCDF measurements data ^{viii}

Country	Use of alternative fuel and raw materials?	Concentration of PCDD/PCDF in ng I-TEQ/m ³ ^a	No. 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	Yes	0.0006 – 0.022	4	
South Africa	(Yes)	0.00053 – 0.001	2	
Spain	Yes	0.00695	20	0.014464
Spain Cemex	Yes	0.0013 – 0.016	5	
Spain Cimpor	Yes	0.00039 – 0.039	8	
Taiheiyo	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 - 25.8	~265	<0.216-16.7
Venezuela	Yes	0.0001 – 0.007	5	
Vietnam		0.0095 – 0.014	3	

^a The numbers are either given as the range or the mean value

^b The high numbers from the USA is from measurements done in the 1990's; the number of measurements are approximate.

Sampling and Analysis of PCDD/PCDF^{viii}

Today sampling of PCDD/PCDF is in most cases undertaken by using one of three methods based on (or following that of) US EPA Method 23, the EN 1948-1 and the German VDI Dilution Method 3499 (also an option in EN 1948-1).

PCDD/PCDF analysis is carried out using high resolution mass spectrometry (GC-MS). Quality control procedures are required in each stage of the analysis and recovery spike concentrations associated with both sampling and extraction. The US EPA Method 23 specifies that all recoveries should be between 70% and 130%.

The lower detection limits LOD measured during the validation test of EN 1948 at a municipal solid waste incinerator varied between 0.0001 - 0.0088 ng/m³ for the 17 individual PCDD/F toxic congeners. In the new draft of EN 1948-3 of February 2004, Annex B, the uncertainty for the complete procedure is given to be 30 - 35 % and the external variability is estimated to be ± 0.05 ng I-TEQ/m³ at a mean concentration of 0.035 ng I-TEQ/m³.

A study performed by Environment Canada assessed the variability of sampling and analysis of 53 sets of PCDD/PCDF emission data from 36 combustion facilities and the limit of quantification (LoQ) for PCDD/PCDF was estimated to be 0.032 ng/m³ TEQ^{viii}, although the LoQ may vary depending on sampling volume, interfering substances and other factors.

3.4 Emissions of HCB and PCB

Hexachlorobenzene and PCB are not subject to regulatory monitoring in cement plants. However, some measurements have revealed that HCB could not be detected, i.e. HCB emission is most probably not an issue for the cement industry. 40 measurements of PCB done in 13 kilns in Germany in 2001 revealed a maximum concentration of 0.4 µg/Nm³; in nine measurements, no PCB was detected^{viii}.

3.5 Other releases of PCDD/PCDF

Due to the high temperatures involved in the cement production process PCDD and PCDF concentrations in solid residues are low. Within a European research project^{xix} samples from a settling chamber and an electrostatic precipitator of a cement kiln were investigated. The dust sample from the settling chamber showed a concentration of 0.4 ng/g PCDD and 0.98 ng/g PCDF. The material from the electrostatic precipitator contained 2.6 ng/g PCDD and 0.4 ng/g PCDF¹.

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

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 NO_x, SO₂, particles, metals).
- (4) Development of environmental monitoring (establishing standard monitoring protocols).

¹ Toxicity equivalents are not indicated.

- (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.
- (8) Occupational health and safety provisions: Cement kilns feeding waste need to have appropriate practices to protect workers on the handling of those materials (not issue once fed to the kiln).
- (9) Sufficient qualification and training of staff.

4.2 Specific measures

New installations / major reconstruction of existing installations

The cement production process has an impact on the energy use and air emissions and for new plants and major upgrades the best available technique for the production of cement clinker is considered to be a dry process kiln with multi-stage preheating and precalcination. For existing installations partially considerable reconstruction is needed ².

Control of the unintentional release of POP (UPOP control): Indirect measure, minor effective for UPOPs reduction in specific cases but element of an integrated concept.

4.2.1 Primary measures and process optimization to reduce PCDD/PCDF ^{xx}

Process optimization

- Characterize a good operation and use this as a basis to improve other operational performance. 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.
- 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.

² 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.

- Minimizing electrical energy use by means of:
 - power management systems;
 - grinding equipment and other electricity based equipment with high energy efficiency.

UPOP control: Indirect measures, minor effective for UPOPs reduction in specific cases but elements of an integrated concept; generally applicable, simple technical construction.

Feed material preparation

- Pre-treatment of waste (waste specific) with the objective to provide a more homogeneous feed and more stable combustion conditions:
 - Drying
 - Shreddering
 - Mixing
 - Grinding
- Well maintained and appropriate storage of fuel.
- Well maintained and appropriate storage and handling of wastes and sites.

UPOP control: Not specific for UPOPs, but elements of an integrated concept.

Input controls

- Consistent long term supply of secondary feeds and waste (supplies of a month or more) is required to maintain stable conditions in the operation.
- Careful selection and control of substances entering the kiln, to minimize introduction of sulfur, nitrogen, chlorine, metals and volatile organic compounds.
- Continuous supply of fuel and waste with specification of
 - Heavy metals,
 - Chlorine (limitation, product/ process dependent),
 - Sulfur.
- Feeding of waste through the main burner or the secondary burner at precalciner/pre-heater kilns [ensure temperature > 900°C].
- No waste feed as part of raw-mix if it includes organics.
- No waste feed during start-up and shut down.

UPOP control: Indirect measures, minor effective for UPOPs reduction in specific cases but elements of an integrated concept; generally applicable, **simple** technical construction. UPOP-formation is possible within relevant temperature ranges.

Stabilisation of process parameters

- Regularity in fuel characteristics (both alternative and fossil)
- Regular dosage
- Excess oxygen
- Monitoring of CO

UPOP control: Indirect measures, minor effective for UPOPs reduction in specific cases but elements of an integrated concept; generally applicable; Is to be ensured to stabilize operating conditions.

Process modification

- Quick cooling of kiln exhaust gases lower than 200°C. The critical range of temperature is usually passed through quickly in the clinker process. Efficiency of this measure could be low and technically highly demanding if existing plants have to be retrofitted.
- 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.

UPOP control: Indirect measures, minor effective for UPOPs reduction in specific cases but elements of an integrated concept.

In general, the primary measures mentioned above are sufficient to comply the 0.1 ng TEQ/Nm³ level in flue gases for new and existing installations. Monitoring should be done. If all of these options do not lead to a performance lower than 0.1 ng TEQ/Nm³ secondary measures may be considered as given below.

4.2.2 Secondary measures

The secondary measures cited below are installed at cement kilns for other pollution control purposes, but they show a simultaneous effect on UPOPs emissions.

Further improvement of dust abatement and recirculation of dust

UPOP control: Efficiency may decrease with decreasing temperature of dust precipitation; general applicability; **medium** technical construction; capture of UPOPs bound to particles.

Activated carbon filter

High removal efficiency for trace pollutants (> 90 %);

Pollutants such as SO₂, organic compounds, metals, NH₃, NH₄⁺ compounds, HCl, HF and residual dust (after an EP or fabric filter) may be removed from the exhaust gases by adsorption on activated carbon. The only activated carbon filter installed at a cement works in Europe is that at Siggenthal, Switzerland. The Siggenthal kiln is a 4-stage cyclone preheater kiln with a capacity of 2000 tonne clinker/day. Measurements showed high removal efficiencies for SO₂, metals and PCDD/PCDF^{vi}.

UPOP control: General applicability, **demanding** technical construction.

Selective catalytic reduction (SCR)

SCR installations are applied for NO_x control. It reduces NO and NO₂ to N₂ with the help of NH₃ and a catalyst at a temperature range of about 300-400°C which would imply heating of the exhaust gases. Up to now SCR has only been tested on preheater and semi-dry (Lepol) kiln systems, but it might be applicable to other kiln systems as well^{vi}. Its high cost could make this solution not economically viable. The first full-scale plant (Solnhofer Zementwerke) is in operation since the end of 1999^{xxi}.

UPOP control: General applicability, **demanding** technical construction; Improvement of UPOP-control by efficient catalysts.

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/PCDF in flue gases should be < 0,1 ng TEQ/Nm³. Emission levels shall be corrected to 273 K, 101.3 kPa, 10 % O₂ and dry gas.

6. Monitoring

To control kiln process, continuous measurements are recommended for the following parameters^{vi}:

- pressure,
- temperature,
- O₂-content
- NO_x,
- CO, and possibly when the SO_x concentration is high
- SO₂ (it is a developing technique to optimise CO with NO_x 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,
- O₂,
- NO_x,
- SO₂, and
- CO

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

- metals and their compounds,
- TOC,
- HCl,
- HF,
- NH₃, 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

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