

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

3.4. Waste Pre-processing

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

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

153. Liquid waste fuels are normally prepared by blending different wastes with suitable calorific values and chemistry (like spent solvents or used oil). Normally, only simple pre-treatment is necessary (removal of bottoms, sediments and water). In some cases, for example machining oil/emulsion, chemical processes are necessary to remove metallic pollutants and additives. The extent of solid waste processing, such as sorting, crushing, or pelletizing, depends on the specific application.

3.4.1 Design considerations

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

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

156. Operations should be assessed for health and safety risks or concerns to ensure that equipment is safe and to minimize risks of endangering people or installations, or damaging the environment. Appropriate procedures should be used to assess risks or hazards for each stage of the design process. Only competent and qualified personnel should undertake or oversee such hazard and operability studies.

3.4.2 Operational considerations

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

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

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

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

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

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

3.5. Pre-processing Plant Closure/Decommissioning

161. Closure is the period directly after the facility stops its normal operations. During this period the facility stops accepting hazardous waste; completes storage and processing of any wastes left on site; and disposes or decontaminates equipment, structures, and soils, restoring the site, insofar as possible, to its original condition or in keeping with the intended land use. Planning for decommissioning of the facility should be undertaken during the initial stages of the overall project. By integrating decommissioning requirements into the facility design at the outset, the site development plan should be compatible with the proper closure requirements when the operation of the facility has ended.

162. Operators should be required to close the facility in a manner that minimizes the further need for maintenance, and prevents the escape of any hazardous contaminants to the environment. To ensure that the facility is properly closed, a closure plan should be prepared identifying the steps necessary to partially or completely close de facility, including:

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

163. To prevent a facility from ceasing operations and failing to provide for the potentially costly closure requirements, operators should be required to demonstrate that they have the financial resources to properly conduct closure in a manner that protects human health and the environment.

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

3.6. Environmental Aspects

3.6.1 VOC, odours, and dust

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

166. Abatement techniques should be in place as needed. Dust is usually reduced by bag filters. Countermeasures for noise and odours should be considered. Common emission control methods for VOC,

pending monitoring results, may include carbon adsorption, thermal treatment and, in specific cases, biological treatment, among others.

3.6.2 Drums and ferrous metals

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

3.6.3 Wastewater

168. Discharges of wastewater to surface water should not result in contaminant concentrations in excess of local ambient water quality criteria or, in the absence of local criteria, other sources of ambient water quality. Receiving water use and assimilative capacity, taking other sources of discharges to the receiving water into consideration, should also influence the acceptable pollution loadings and effluent discharge quality.

169. Discharges into public or private wastewater treatment systems should meet the pre-treatment and monitoring requirements of the sewer treatment system into which it discharges, and should not interfere, directly or indirectly, with the operation and maintenance of the collection and treatment systems, or pose a risk to worker health and safety, or adversely impact characteristics of residuals from wastewater treatment operations.

3.7. Emissions Monitoring and Reporting

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

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

172. The parameters selected for monitoring should be indicative of the pollutants of concern from the process, and should include parameters that are regulated under compliance requirements. Monitoring programmes should apply national or international methods for sample collection and analysis, such as those published by the International Organization for Standardization (ISO), CEN or the United States EPA. Sampling should be conducted by, or under, the supervision of trained individuals. Analysis should be conducted by entities permitted or certified for this purpose. Sampling and analysis QA/QC plans should be applied and documented to ensure that data quality is adequate for the intended data use. Monitoring reports should include QA/QC documentation.

173. More useful information regarding monitoring principles can be found in the European Commission's Reference Document on the General Principles of Monitoring, which presents the results of an exchange of information carried out under Council Directive 2008/1/EC between EU Member States and the industries concerned (EIPPCB, 2003). Good practice for reporting monitoring results is described in Section 4.4.4 of these Guidelines.

4. Co-processing in Cement Kilns

4.1. Introduction

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

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

- The alkaline conditions and the intensive mixing favour the absorption of volatile components from the gas phase. This internal gas cleaning results in low emissions of components such as SO₂, HCl, and most of the heavy metals, with the exception of mercury, cadmium and thallium.
- The clinker reactions at 1450°C allow the chemical binding of metals and the incorporation of ashes to the clinker.
- The direct substitution of primary fuel by high calorific waste material causes a higher efficiency on energy recovery in comparison to other 'waste to energy' technologies (destruction of organics).

4.2. Operational Requirements

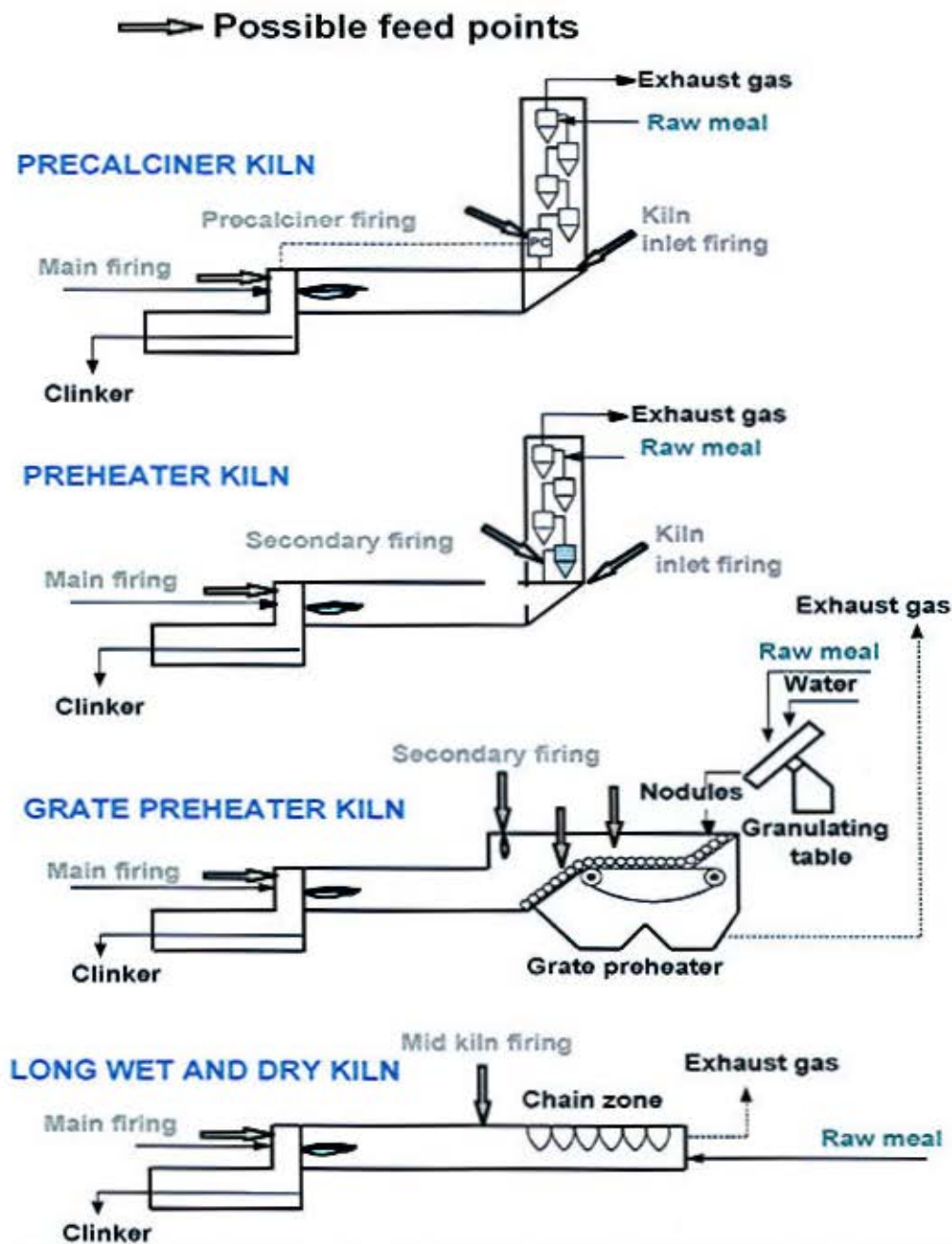
176. Safe and responsible co-processing requires careful selection of the feed points in the kiln system as well as comprehensive operational control according to the specific characteristics and volumes of the waste material.

4.2.1 Feed point selection

177. Adequate feed points should be selected according to the physical, chemical, and (if relevant) toxicological characteristics of the waste material used (see Figure 3). Different feed points can be used to introduce waste materials into the cement production process. The most common ones being:

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

Figure 3. Typical waste feed points



178. Liquid wastes are typically injected into the hot end of the kiln. Solid wastes may be introduced into the calcining zone at some facilities. For long kilns, this means that the solid waste is introduced mid-kiln, and for preheater/precalciner kilns that it is introduced onto the feed shelf in the high-temperature section.

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

180. Complete destruction of combustible toxic compounds, such as halogenated organic substances, present in hazardous waste needs to be ensured through proper temperature and residence time. In general, hazardous

waste should be fed through either the main burner or the secondary burner for preheater/precalciner kilns. In the former, conditions will always be favourable. Hazardous and other wastes fed through the main burner will be decomposed under oxidising conditions at a flame temperature of $>1800^{\circ}\text{C}$ (see Figure 4); waste fed to a secondary burner, preheater or precalciner will be exposed to lower temperatures, though expected burning zone temperatures in the precalciner are typically $>1000^{\circ}\text{C}$ (UNEP, 2007). Under the Council Directive 2000/76/EC, the kiln needs to be operated in such a way that the gas resulting from the process is raised, after the last injection of combustion air, in a controlled and homogeneous fashion and even under the most unfavourable conditions, to a temperature of 850°C for two seconds. In the case of hazardous wastes with a content of more than 1 percent halogenated organic substances (expressed as chlorine), the temperature needs to be raised to 1100°C for at least two seconds. Under the United States TSCA disposal of PCBs requires a temperature of 1200°C and 2 seconds retention time (at 3 percent excess oxygen in the stack gas).

Figure 4: Temperatures and residence times during cement manufacture

Characteristics	Temperature and time	
Temperature at main burner ① of the rotary kiln ②	$>1450^{\circ}\text{C}$ (material) $>1800^{\circ}\text{C}$ (flame temperature)	
Residence time at main burner	$>12\text{-}15$ seconds $> 1200^{\circ}\text{C}$ $>5\text{-}6$ seconds $> 1800^{\circ}\text{C}$	
Temperature at precalciner ③	$> 850^{\circ}\text{C}$ (material) $>1000^{\circ}\text{C}$ (flame temperature)	
Residence time at precalciner	$> 2\text{-}6$ seconds $> 800^{\circ}\text{C}$	

181. In the EU, the BAT conclusion for waste feeding into the kiln, applicable to cement kilns co-processing hazardous waste, is (EIPPCB, 2010):

- To use the appropriate feed points to the kiln in terms of temperature and residence time depending on kiln design and kiln operation;
- To feed waste materials containing organic components that can be volatilised before the calcining zone into the adequately high temperature zones of the kiln system;
- To operate in such a way that the gas resulting from the process is raised, in a controlled and homogeneous fashion and even under the most unfavourable conditions, to a temperature of 850°C for 2 seconds;
- To raise the temperature to 1100°C , if hazardous waste with a content of more than 1 percent of halogenated organic substances, expressed as chlorine, is fed into the kiln;
- To feed wastes continuously and constantly; and
- To stop feeding waste for operations such as start-ups and/or shutdowns when appropriate temperatures and residence times cannot be reached.

4.2.2 Kiln operation control

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

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

184. For upset conditions of the kiln, written work instructions describing the strategy to disconnect the hazardous waste feed to ensure minimum operational stability conditions should be available and known to the kiln operators.

185. The mineral content of the waste may change the characteristics of the clinker. The raw mix composition ought to be adjusted accordingly to stick to the given chemical set points. Input limits for chlorine, sulphur, and alkalis should be defined, and operational set points should be strictly observed. Bypass installations to avoid alkalis, sulphur and chlorine enrichment cycles should only be considered if appropriate solutions for the management of the bypass dust generated have been identified.

186. It is important for combustion and process stability, for the purpose of controlling emissions of unintentionally formed POPs, to ensure (UNEP, 2007):

- 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.

4.3. Environmental Aspects

4.3.1 Air emissions

187. The main emissions from cement kiln systems are emissions to air, whether alternative fuels and/or raw materials are being used or not. Emissions that have been identified as relevant are dust (particulate matter), NO_x and other nitrogen compounds, CO, CO₂, SO₂ and other oxides of sulphur, metals and their compounds, HCl, HF, PCDDs, PCDFs, and total organic compounds (TOC) (EIPPCB, 2010). More specifically, emissions may include, inter alia, ammonia (NH₃), benzene, toluene, xylene, polycyclic aromatic hydrocarbons (PAH), chlorobenzenes and PCBs (SBC, 2007). The sources of these emissions are outlined in Annex 4.

188. Existing and potential control technologies are described by Greer (2003) and Karstensen (2008b), while details on BAT and associated emission levels in the EU are provided by the EIPPCB (2010). The European Commission's reference document includes information regarding available measures/techniques, such as description, applicability, cross-media effects, economics, etc., and provides useful information along with best performance data on techniques to be considered as BAT.

189. Furthermore, guidance on BAT and provisional guidance on BEP for the prevention or minimization of the formation and subsequent release of unintentional POPs from cement kilns co-processing hazardous waste has been published by the Stockholm Convention Secretariat (UNEP, 2007). The said guidelines describes primary measures considered to be sufficient to achieve an emission level of PCDDs/PCDFs below 0.1 ng I-TEQ/Nm³ in flue gases for new and existing installations, and where these options do not lead to performance down to 0.1 ng I-TEQ/Nm³, secondary measures are cited, which are usually installed for the purpose of controlling pollutants other than unintentionally formed POPs, but that may also lead to a simultaneous reduction in emissions of chemicals listed in Annex C. (UNEP, 2007)

190. For information purposes, examples of emission limits applicable to cement kilns co-processing hazardous wastes are provided in Annex 5. Competent authorities should consider establishing a maximum permissible period of any technically unavoidable stoppages, disturbances, or failures of the purification devices or the measurement devices, during which the emissions into the air may exceed the prescribed emission limit values.

4.3.2 Cement kiln and bypass dust

191. All cement plants generate a fine dust from the kiln line, collectively labelled CKD. CKD composition varies among plants and even over time from a single kiln line, but includes particulates representing the raw mix at various stages of burning, particles of clinker, and even particles eroded from the refractory brick and/or

monolithic linings of the kiln tube and associated apparatus (Van Oss, 2005). Dust is also discarded from alkali bypass systems (installed to avoid excessive build-up of alkali, chloride and/or sulphur), however bypass dust, as opposed to CKD, consists of fully calcined kiln feed material.

192. In the EU, the BAT conclusion for process waste, in the cement manufacturing sector in general, is to re-use collected particulate matter in the process, wherever practicable, or to utilise these dusts in other commercial products, when possible. (EIPPCB, 2010)

193. The majority of CKD and bypass dust is recycled directly back to the cement kiln and/or cement clinker grinder, thus avoiding disposal. In clinker manufacture, CKD partially offsets the need for raw material feed, such as limestone and natural constituents (rock), thus avoiding the energy usage and emissions related to their extraction and processing. However, some dust may need to be periodically removed from the system due to increasing concentrations of alkali, chloride and sulphur compounds that may compromise the quality of the clinker. Dust that cannot be recycled back into the process is removed from the system and often collected onsite in piles or monofills.

194. The U.S. EPA (2010) reports that CKD not returned to the production process can be sold for various types of commercial applications, including agricultural soil enhancement, base stabilizing for pavements, wastewater treatment, waste remediation, low-strength backfill and municipal landfill cover. These applications depend primarily on the chemical and physical characteristics of the CKD. The major parameters that determine CKD characteristics are the raw feed material, type of kiln operation, dust collection systems, and fuel type. Since the properties of CKD can be significantly affected by the design, operation, and materials used in a cement kiln, the chemical and physical characteristics of CKD must be evaluated on an individual plant basis. (U.S. EPA, 2010) Until the degree of variability in the CKD has been established, frequent testing is recommended.

195. Depending upon the level of contaminants of concern (for example, heavy metals, POPs), 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 (UNEP, 2007). A study by Karstensen (2006b) reports an average concentration of 6.7 ng I-TEQ/kg for PCDDs/PCDFs in CKD and a maximum concentration of 96 ng I-TEQ/kg. The same study shows that wastes from the cement industry have dioxin levels in the same magnitude as foods like fish, butter, breast milk, and less than the maximum permissible concentration of 100 ng TEQ/kg for sewage sludge applied to agricultural land.

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

4.3.3 End-product control

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

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

199. Organic pollutants in the materials fed to the high temperature zone of the kiln system are completely destroyed, while the inorganic components are incorporated into the end product. Accordingly, the use of wastes in the clinker burning process may change the metal concentrations in cement products, and depending on the total input via the raw materials and fuels, the concentration of individual elements in the product may increase or decrease as a result of waste co-processing (EIPPCB, 2010). However, lengthy investigations have shown that the effect of waste on the heavy metals content of clinker is marginal on a statistical basis, the one exception being the bulk use of tires which will raise zinc levels (GTZ/Holcim, 2006).

200. As cement is blended with aggregates for the production of concrete or mortar, it is the behaviour of the metals in the building material (concrete or mortar) which is ultimately decisive for evaluating the environmentally relevant impacts of waste used in the clinker burning process (EIPPCB, 2010). In this regard, the main results of leaching studies done to assess the environmental impacts of heavy metals embedded in concrete are as follows (GTZ/Holcim, 2006):

- The leached amounts of all trace elements from monolithic concrete (service life and recycling) are below or close the detection limits of the most sensitive analytical methods;
- No significant differences in leaching behaviour of trace elements have been observed between different types of cements produced with or without alternative fuels and raw materials;
- The leaching behaviour of concrete made with different cement types is similar;
- Leached concentrations of some elements such as chromium, aluminium and barium may, under certain test conditions, come close to limits given in drinking water standards; hexavalent chromium in cement is water-soluble and may be leached from concrete at a level higher than other metals, so chromium inputs to cement and concrete should be as limited as possible;
- Laboratory tests and field studies have demonstrated that applicable limit values (for example, groundwater or drinking water specifications) are not exceeded as long as the concrete structure remains intact (for example, in primary or service life applications);
- Certain metals such as arsenic, chromium, vanadium, antimony, or molybdenum may have a more mobile leaching behaviour, especially when the mortar or concrete structure is crushed or comminuted (for example, in recycling stages such as use as aggregates in road foundations, or in end-of-life scenarios such as landfilling); and
- As there are no simple and consistent relations between the leached amounts of trace elements and their total concentrations in concrete or in cement, the trace element content of cements cannot be used as environmental criteria.

201. Assessments of the environmental quality of cement and concrete are typically based on the leaching characteristics of heavy metals to water and soil. Various exposure scenarios need to be considered (GTZ/Holcim, 2006):

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

202. Careful selection and monitoring of the waste materials ensure that the use of wastes does not result in metal emissions of any environmentally harmful magnitude (EIPPCB, 2010). However, in cases where the concentration of heavy metals exceeds the normal range found in cements made without alternative fuels and/or materials, leaching tests on mortar and/or concrete should be conducted (GTZ/Holcim, 2006).

203. For different "real-life" concrete and mortar exposure scenarios, different leaching tests and assessment procedures need to be applied. Existing standardized test procedures have been developed mainly for use in relation to waste management regulations and drinking water standards, however there remains a need for harmonized and standardized compliance test procedures based on the exposure scenarios outlined above. It is recommended that these tests be performed at least annually by a certified independent testing laboratory.

4.4. Monitoring

204. Emission monitoring is necessary to allow authorities to check compliance with the conditions in operating permits and regulations, and to help operators manage and control the process, thus preventing emissions from being released into the atmosphere. It is the responsibility of the competent authority to establish and set appropriate quality requirements, and to consider a range of safeguards. For the purpose of compliance assessment use of the following is considered good practice (EIPPCB, 2003):

- Standard methods of measurement;
- Certified instruments;

- Certification of personnel; and
- Accredited laboratories.

205. For self-monitoring activities the use of recognised quality management systems and periodic check by an external accredited laboratory instead of formal own accreditation can be appropriate (EIPPCB, 2003).

206. More useful information regarding monitoring principles can be found in the European Commission's Reference Document on the General Principles of Monitoring (EIPPCB, 2003).

4.4.1 Process monitoring

207. To control kiln processes, continuous measurements are recommended for the following parameters (UNEP, 2007; EIPPCB, 2010):

- Pressure
- Temperature
- O₂
- 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).

208. In the EU, the BAT conclusion for the cement manufacturing sector as a whole is to carry out monitoring and measurements of process parameters and emissions on a regular basis, such as (EIPPCB, 2010):

- Continuous measurements of process parameters demonstrating process stability, such as temperature, O₂, pressure, exhaust gas flow rate, and of NH₃ emissions when using selective non-catalytic reduction (SNCR); and
- Monitoring and stabilising critical process parameters, for example, homogenous raw material mix and fuel feed, regular dosage and excess O₂.

4.4.2 Emissions monitoring

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

- Exhaust gas flow rate
- Moisture (humidity)
- Temperature
- Dust (particulate matter)
- O₂
- NO_x
- SO₂
- CO

210. Further to the above, continuous measurement of TOC is recommended. The operator should assure proper calibration, maintenance, and operation of the continuous emission monitoring systems (CEMS). A quality assurance programme should be established to evaluate and monitor CEMS performance on a continual basis.

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

- Metals (Hg, Cd, Tl, As, Sb, Pb, Cr, Co, Cu, Mn, Ni, V) and their compounds
- HCl
- HF
- NH₃
- PCDDs/PCDFs

212. The BAT considered to be appropriate to the European cement manufacturing sector in general is to carry out monitoring and measurements of process parameters and emissions on a regular basis, such as (EIPPCB, 2010):

- Continuous measurements of dust, NO_x, SO_x and CO emissions;
- Periodic measurements of PCDDs/PCDFs and metals emissions; and
- Continuous or periodic measurements of HCl, HF and TOC emissions.

213. In addition, cement kilns co-processing hazardous and other wastes in the EU should comply with the relevant requirements under Directive 2000/76/EC.

214. It is also possible to measure and monitor NH₃ and Hg continuously, and to sample PCDDs/PCDFs and PCBs continuously for analysis from 1 to 30 days (EIPPCB, 2010).

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

216. Measurements of the following may be required under special operating conditions (UNEP, 2007; EIPPCB, 2010):

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

217. In case of hazardous waste disposal in cement kilns for the purpose of destruction and irreversible transformation of the POPs content in waste, the DRE should be determined (UNEP, 2007).

4.4.3 Environmental monitoring

218. Where there are justifiable concerns, an ambient air-monitoring programme may be required to monitor the environmental impact from the plant. This should assess environmental levels of key pollutants identified as a priority for control. The arrangements should include control and downwind locations, including the area of maximum ground level deposition from stack emissions. A meteorological station should be provided for the duration of the ambient sampling exercise in a location free of significant interference from buildings or other structures.

4.4.4 Reporting requirements

219. Reporting of monitoring results involves summarising and presenting results, related information and compliance findings in an effective way. Good practice is based on consideration of: the requirements and audiences for reports, responsibilities for producing reports, the categories of reports, scope of reports, good reporting practices, legal aspects of reporting and quality considerations (EIPPCB, 2003)

220. Monitoring reports can be classified as follows (EIPPCB, 2003):

- Local or basic reports, which are usually prepared by operators (for example, as part of their self-monitoring) and, where appropriate, should meet any permit requirements. These reports may concern,

for example, an individual installation, an occurrence which covers a short period and needs to be reported promptly, or local audiences.

- National or strategic reports, which will generally be prepared by the competent authorities. These are usually summary reports and they typically concern, for example, several installations, longer periods in order to show trends, or national audiences.
- Specialised reports, which are reports on relatively complex or novel techniques that are occasionally used to supplement more routine monitoring methods (for example, telemetry, neural networks, or deposition surveys).

221. Good practices in the reporting of monitoring information include (EIPPCB, 2003):

- Data collection, which involves the acquisition of basic measurements and facts. Considerations of the following items are good practice in data collection: schedules (stating how, when, by whom and to whom the data are to be reported, and what types of data are acceptable); use of standard forms for collecting data; data qualification details (used to record whether data values are based on measurements, calculations or estimations); uncertainties and limitations data (details of detection limits, numbers of samples available); operational context details (details of the prevailing process operations and/or environmental conditions).
- Data management, involving the organisation of data and its conversion into information. Considerations of the following items are good practice in data management: transfers and databases; data processing; software and statistics; and archiving.
- Presentation of results, which involves the delivery of information to users in a clear and usable form. Considerations of the following items are good practice in the presentation of monitoring results, depending on the type of report: scope of the report (type of situation, timing requirements, location); programme of presentations; trends and comparisons; statistical significance (details on exceedences or changes that are significant when compared with the uncertainties in measurements and process parameters); interim performance (interim reports); strategic results (details on levels of compliance for different policies, activities, technologies, etc.); non-technical summaries (for the public); and distribution of reports.

222. In order for monitoring reports to be used in decision making processes they need to be readily available and accurate (to within stated uncertainties). Good practice in accessibility and quality of the reports can be achieved by considering the following items: quality objectives and checks; competence; contingency arrangements; sign-off systems; retention of data; and falsification of data. (EIPPCB, 2003)

223. More useful information on monitoring principles can be found in the European Commission's Reference Document on the General Principles of Monitoring (EIPPCB, 2003).

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Annex 1. Clinker Production Process

1. Cement production involves the heating, calcining and sintering of a carefully proportioned mixture of calcareous and argillaceous materials, usually limestone and clay, to produce cement clinker, which is then cooled and ground with additives such as gypsum (a setting retardant) to make cement. This process typically requires approximately 2,9 to 6,7 GJ of energy depending on the kiln technology employed (IEA, 2007) and 1,5 to 1,7 tonnes of raw materials per tonne of clinker produced (Szabó et al, 2003); the portion of raw material that does not become clinker is either lost on ignition or becomes CKD (U.S. EPA, 1993). 'Wet' processes also use water to make the raw slurry that feeds the kilns; about 600 kg of water is used in the manufacture of one tonne of cement, some of which is returned to the environment (EA, 2005).
2. Manufacturers use clinker and specific constituents in various proportions to produce cements that meet different physical and chemical requirements for specific applications. By far the most common hydraulic cements in use today are either Portland cements or 'blended' cements (van Oss and Padovani, 2003). The standard specifications with which Portland cements must comply are similar (albeit not identical) in all countries and various names are used to define the material. Blended cements, also called composite cements, are mixtures of Portland cement with one or more pozzolanic additives or extenders (sometimes collectively termed 'supplementary cementitious materials'), such as pozzolana (volcanic ashes), certain types of fly ash (from coal-fired powerplants), granulated blast furnace slag, silica fume, or limestone. These materials commonly make up about 5% to 30% by weight of the total blend, but can be higher (van Oss, 2005). The designations for blended cements differ worldwide.
3. Although a variety of cement types are produced worldwide, cement production follows essentially the same process, as described below.

Conventional Raw Materials and Fuel

4. The raw materials for cement must yield the oxides required for clinker in the approximate proportions noted in Table 1, with the major requirement being calcium oxide (CaO). In practical terms this means that naturally occurring calcareous deposits, such as limestone, marl or chalk, which consist essentially of calcium carbonate (CaCO₃), are required. Clay or shale typically provides the remaining components. To correct for minor deficiencies in one or more oxides in the primary raw materials, 'corrective' constituents⁹ such as iron ore, bauxite or sand, may be added to adapt the chemical composition of the raw mix to the requirements of the process and product specifications (Taylor, 1997; Karstensen, 2007b). Generally, most, but not all, of the raw materials are mined adjacent to or within a few miles of the cement plant.

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

Constituent	Clinker	Limestone, lime marl, chalk	Clay	Sand	Iron ore	Bauxite
SiO ₂	19,71-24,25%	0,5-50%	33-78%	80-99%	4-11%	2,9%
Al ₂ O ₃	3,76-6,78%	0,1-20%	7-30%	0,5-7%		
TiO ₂	0,21-0,52%	0,0-0,7%	0,2-1,8%	0,0-0,5%		
Al ₂ O ₃ + TiO ₂			7-30%	0,5-2%	0,2-3%	57,5%
Fe ₂ O ₃	1,29-4,64%	0,2-5,9%	4,0-15%	0,0-4%		
Mn ₂ O ₃	0,03-0,68%	0,02-0,15%	0,09%	0,051%		
Fe ₂ O ₃ + Mn ₂ O ₃		0,1-10%	2-15%	0,5-2%	19-95%	22,8%
CaO	63,76-70,14%	20-55%	0,2-25%	0,1-3%	0,1-34%	2,4%

⁹ Sometimes called accessory or 'sweetener' materials (van Oss, 2005).

Constituent	Clinker	Limestone, lime marl, chalk	Clay	Sand	Iron ore	Bauxite
MgO	0,00-4,51%	0,2-6%	0,3-5%	0,3-0,5%	≤1,5%	0,04%
K ₂ O	0,31-1,76%	0-3,5%	0,4-5%	0,2-3%	Traces	0,04%
Na ₂ O	0,03-0,335	0,0-1,5%	0,1-1,5%	0,0-1%	Traces	0,02%
Cl		0,0-0,6%	0,0-1%	Traces		
P ₂ O ₅	0,02-0,27%	0,0-0,8%	0,0-1,0%	0,0-0,1%		
Loss on ignition (CO ₂ + H ₂ O)	0,09-1,56%	2-44%	1-20%	≤5	0,1-30%	13,5%

Sources: EIPPCB (2010) and CEMBUREAU (1999)

5. Natural forms of CaCO₃ consist of coarser or finer crystals of calcite. Limestone is microcrystalline CaCO₃ with clay as the main impurity. Chalk is a very fine grained, porous marine limestone composed almost entirely of microscopic fossils. The main constituents of shale and clay are clay minerals, finely divided quartz and, sometimes, iron oxides. Traditionally, wet materials (chalk and clay) have been used in 'wet' or 'semi-wet' kiln processes, and dry materials (limestone) have been used in the 'dry' or 'semi-dry' processes (EA, 2005).

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

7. The proportioning process takes into account the ratios of calcium, silica (SiO₂), alumina (Al₂O₃), and iron oxide (Fe₂O₃) needed to produce good quality clinker, as well as the 'burnability' of the raw mix (i.e., the requirements in terms of time, temperature, and fuel to process the material) (U.S. EPA, 1993). In addition, kiln operators pay close attention to the presence of 'impurities' in the mixture, including magnesia, sulphur, chlorides, and oxides of potassium and sodium (referred to as 'alkalies'). Magnesia (MgO) can be desirable to some extent because it acts as a flux at sintering temperatures, facilitating the burning process, however MgO levels are carefully monitored because they can lead to the production of clinker that is unsound if not cooled rapidly¹⁰. Alkalies can react in the cool end of the kiln with sulphur dioxide, chlorides, and carbon dioxide contained in the kiln gas and can lead to operational problems (U.S. EPA, 1993).

8. The raw materials used in the cement production process naturally contain metals and halogens. Thus, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, thallium, vanadium, zinc, bromine, chlorine, fluorine, and iodine are typically present in the raw materials. The amounts of these components depend on the geological formations from which the raw materials are mined. In addition to the metals and halogens present, the raw materials can contain organic compounds (Mantus, 1992). Average values and range of concentrations of these constituents are presented in Table 2.

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

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

11. Coal can contain significant quantities of sulphur, trace metals, and halogens, and their concentrations are dependent on the area in which the coal was mined (see Table 3). Sulphur (in the form of SO₂) will vaporize in the kiln to form sulphur dioxide (SO₂), and condense in the form of sulphates. Within the kiln, these sulphates combine with calcium and potassium, causing operational problems in the cool end of the kiln. Halogens are of

¹⁰ Such clinker used to make concrete can cause destructive expansion of hardened concrete through slow reaction with water.

concern because chlorides can cause operational problems similar to those caused by sulphur. Chlorine concentrations in coal can range from 100 to 2800 parts per million. (U.S. EPA, 1993)

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

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

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

a/ Mantus (1992)

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

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

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

a/ Mantus (1992)

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

Table 4. Energy requirements for clinker manufacture

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

Source: IEA (2007) and Szabó (2003)

Manufacturing Process

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

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

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

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

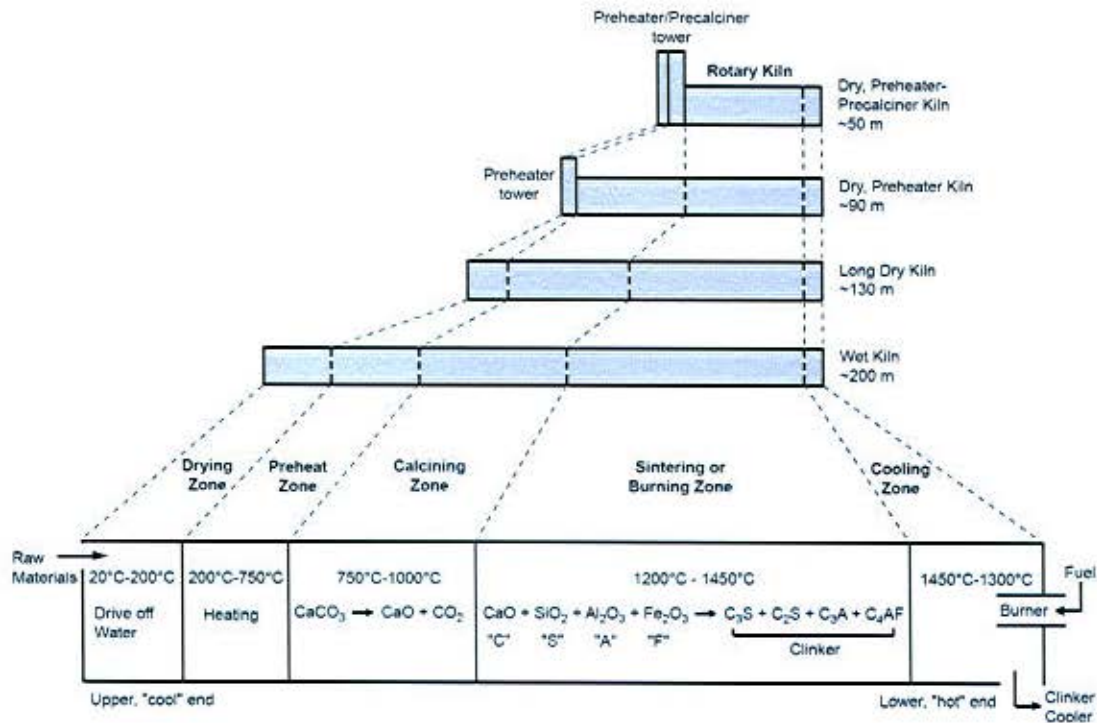
Table 5. Typical mineralogical composition of ordinary Portland cement clinker

Chemical name (common name)	Chemical formula	Common notation ^{a/}	Concentration range
Tricalcium silicate ('alite')	Ca_3SiO_5	C_3S	50-70%
Dicalcium silicate ('belite')	Ca_2SiO_4	C_2S	15-30%
Tricalcium aluminate ('aluminat')	$\text{Ca}_3\text{Al}_2\text{O}_6$	C_3A	5-10%
Tetracalcium aluminoferrite ('ferrite')	$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$	C_4AF	5-15%

^{a/} Abbreviations: C=CaO; S=SiO₂; A=Al₂O₃; F=Fe₂O₃

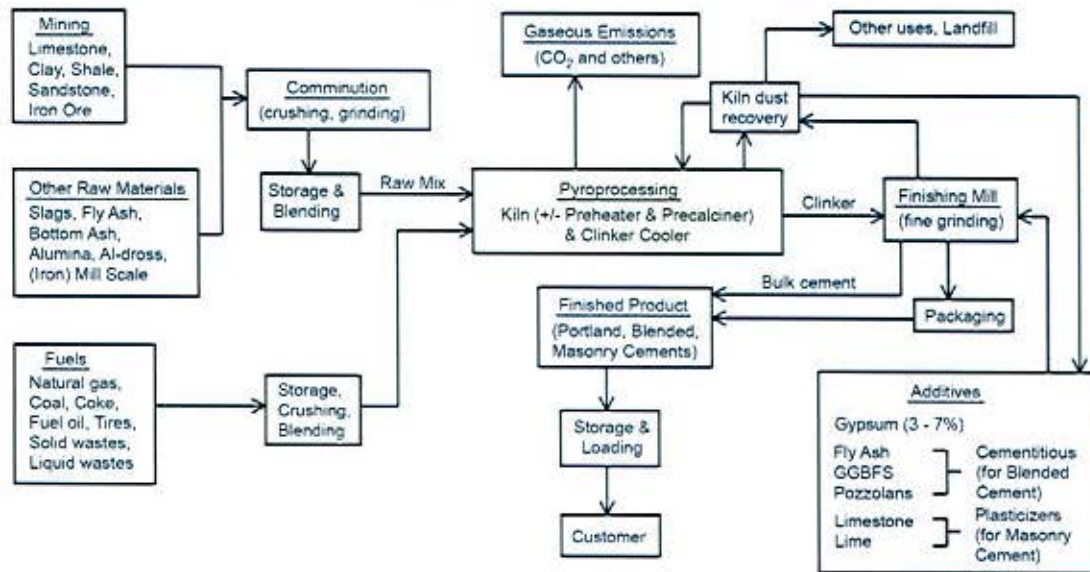
Source: Taylor (1997)

Figure 1. Diagram of 'reaction' zones for different kiln technologies



Source: van Oss (2005)

Figure 2. General cement manufacturing process



Source: van Oss (2005)

17. Clinker can be made either in energy-intensive and small-scale vertical kilns or in more efficient, larger scale rotary kilns. With the exception of vertical shaft kilns (VSK) still used in certain geographical areas (mainly China and India) (CPCB, 2007; Höhne and Ellermann, 2008), cement clinker is predominantly burnt in rotary kilns. For the manufacture of cement using rotary kilns heating of the raw meal to produce cement clinker

can take place in one of four different types of arrangements: the 'dry', 'semi-dry', 'semi-wet', or 'wet' processes (EIPPCB, 2010; UNEP, 2007):

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

18. In China approximately 60 percent of the cement was produced in VSKs, an amount that is expected to drop to 50 percent by 2015 (Karstensen, 2006a). In Europe, about 90 percent of the cement production is from dry process kilns, a further 7.5 percent of production is accounted for by semi-dry and semi-wet process kilns, with the remainder of European production, about 2.5 percent, coming from wet process kilns (EIPPCB, 2010). In the United States, no new wet kilns have been built since 1975, and approximately 80 percent of U.S. cement production capacity now relies on the dry process technology (U.S. Environmental Protection Agency, 2007). The wet process remains dominant in the former Soviet Union and Australia/New Zealand and is still significant in Canada, India, Latin America and Africa (Watson et al., 2005). Table 6 provides the share mix of kiln technologies in each region or country in 2002.

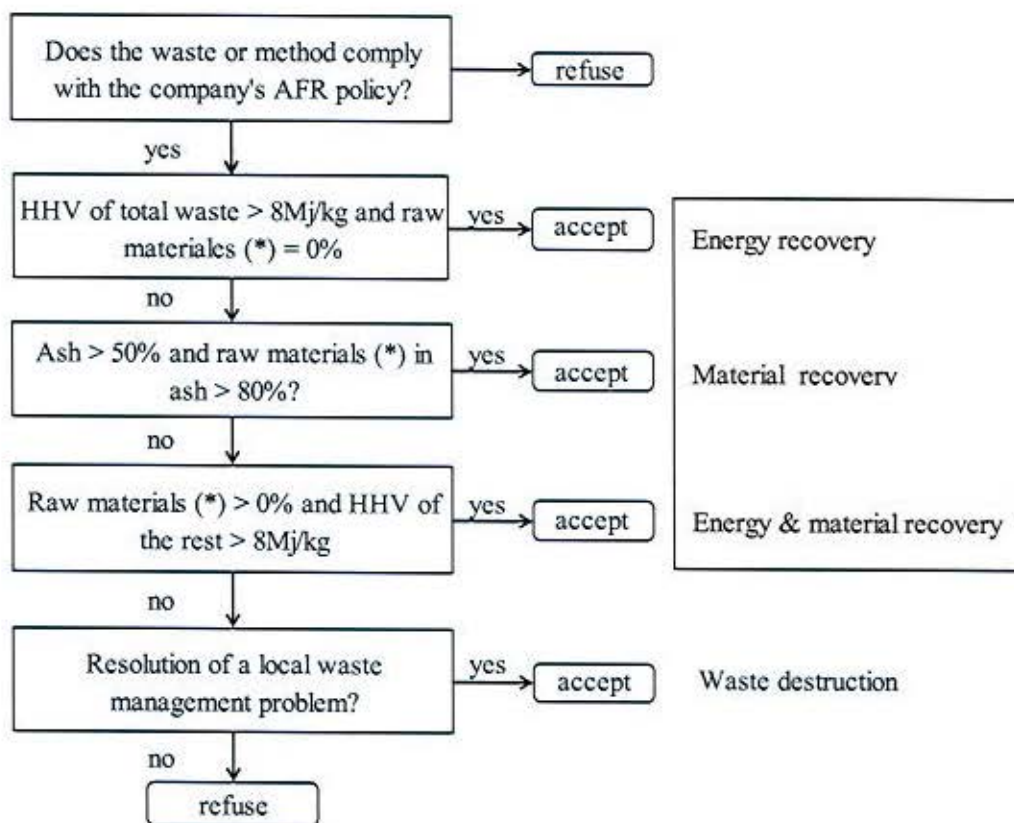
19. Although VSKs are improvements over the old, chimney-type kilns in that some VSKs allow for continuous processing, they are considered to be less energy efficient than the rotary kilns, and VSK clinker (and hence cement) is generally considered to be of lower quality (van Oss, 2005). Furthermore, many VSKs plants have virtually no environmental controls in place, and the nature of the technology precludes effective use of modern dust (and other emission) controls. Compared with preheater/precalciner kilns, VSKs seems to consume from 14 % to 105 % more coal per tonne of clinker; fuel substitution is however not feasible for vertical shaft kilns (Karstensen, 2006a). The raw materials used for cement production in VSKs are exactly the same as in any other production process; corrective materials may also be required to adjust the chemical composition of the raw mix.

Table 6. Share of different kiln types in 2002

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

Source: Baron et al. (2007)

Annex 2. Example of a Waste Acceptance Decision Chart



HHV: Higher heating (calorific) value
 (*) CaO, SiO₂, Al₂O₃, Fe₂O₃, SO₃

Source: GTZ/Holcim (2006)

Annex 3. Compilation of Performance Verification and Test Burns Results in Cement Kilns
(Dr. Kare Helge Karstensen, personal communication, November 6, 2009)

Introduction

20. Testing of cement kiln emissions for the presence of organic chemicals during the burning of hazardous materials has been undertaken since the 1970s, when the practice of combusting wastes in cement kilns was first considered. Lauber (1987), Ahling (1979) and Benestad (1989) describe some of these early tests on U.S., Swedish and Norwegian kilns, which confirmed the ability of cement kilns to destroy the organic component of a waste feed. For example, the DRE for chemicals such as methylene chloride, carbon tetrachloride, trichlorobenzene, trichloroethane and PCBs has typically been measured at 99.995 % and better.

21. Comprehensive emission studies have been performed when a conventional fuel such as coal was burned, and when hazardous waste was introduced, and these have generally concluded that no significant differences could be measured between usages of the two fuels. For example, Branscome et al (1985) observed that "no statistically significant increase in emission rates were observed when the waste fuel (as opposed to coal) was burned". Early studies on dioxin emissions have also come to this conclusion (Branscome et al. (1985), Lauber (1987) and Garg (1990)).

Results from trial burns conducted in the 1970s

22. In the mid-1970s, a series of tests were conducted at the St. Lawrence cement plant in Canada to measure the destruction of various chlorinated waste streams being fed into their wet process cement kiln. The overall DRE established for the chlorinated compounds was greater than 99.986 %. This value was considered to be artificially low because the water used to slurry the raw feed was contaminated with low molecular weight chlorinated compounds.

23. In 1978, a series of tests was conducted at the Stora Vika Cement Plant in Sweden to evaluate the efficiency of their wet process cement kiln in destroying various chlorinated waste streams. Although chloroform was found in the stack gas, the majority of the chlorinated compounds were not detected. A DRE greater than 99.995 % was determined for methylene chloride and a DRE greater than 99.9998 % was demonstrated for trichloroethylene.

Results from trial burns conducted in the 1980s

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

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

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

Results from trial burns conducted in the 1990s

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

26. In a DRE testing of a dry process cement kiln equipped with a preheater, carbon tetrachloride and trichlorobenzene were chosen as the POHCs. When fed to the burning zone of the kiln, DREs obtained were

greater than 99.999 % for carbon tetrachloride and greater than 99.995 % for trichlorobenzene. To determine the limits of the system, DREs were also determined when these POHCs were fed to the kiln inlet (i.e. cool end) of the kiln along with tyres. DREs obtained were greater than 99.999 % for carbon tetrachloride and greater than 99.996 % for trichlorobenzene.

27. DRE testing conducted at a cement kiln owned by United Cement supports the foregoing results. Sulphur hexafluoride was chosen as the POHC because of its thermal stability and ease of measurement in the stack gases. In addition, "contamination" problems and PIC interferences are unlikely with the use of this compound. DREs greater than 99.9998 % were obtained in every case.

28. In 1999 a test burn with pesticide contaminated soil fed into the kiln inlet was performed in a dry process kiln in Colombia. The test burn result showed a DRE of >99.9999 % for all the introduced pesticides.

Results from recent trial burns

29. A test burn with two expired chlorinated insecticide compounds introduced at a rate of 2 tons per hour through the main burner was carried out in Vietnam in 2003. The DRE for the introduced insecticides was >99.99999 %.

30. A three day test burn in Sri Lanka in 2006 demonstrated that the cement kiln was able to destroy PCB in an irreversible and environmental sound manner without causing any new formation of PCDD/PCDF or HCB. The destruction and removal efficiency (DRE) was better than 99.9999% at the highest PCB feeding rate.

31. A five day test burn with POPs contaminated soil was conducted in a cement kiln in Venezuela in 2007. The soil was contaminated with relatively low levels of various chlorinated pesticides, first of all the aldrin, dieldrin and endrin (up to max 551 mg/kg). Measurement showed the same low levels of dieldrin in the stack gas ($<0.019 \mu\text{g}/\text{Nm}^3$) when no contaminated soil was fed as when feeding 2 tonne/h of contaminated soil containing up to 522 mg dieldrin/kg. It can therefore be assumed that the measured DRE of 99.9994 % achieved with the highest feeding concentration is probably higher in reality.

32. A recent study evaluating more than 2000 PCDD/PCDF cement kiln measurements and indicating that most modern cement kilns co-processing waste (also organic hazardous wastes) can meet an emission level of $0.1 \text{ ng PCDD/PCDF I-TEQ}/\text{m}^3$.

Summary

33. Earlier data which indicated cement kiln DRE results below 99.99 % are most probably either from outdated sources or improperly designed tests, or both. In the early years of development of this concept and the sampling and analytical techniques to evaluate its environmental performance, there were several instances where POHCs were selected that did not meet the necessary criteria. For example, a major problem with many early tests was that the POHCs selected for DRE evaluation were organic species that are typically found at trace levels in the stack emissions from cement kilns that burn solely fossil fuel. While these PICs were emitted at very low levels, they nonetheless greatly interfered with the measurement of POHC destruction. Practitioners quickly learned that DRE could not be properly measured if POHCs used in testing were chemically the same or closely related to the type of PICs routinely emitted from raw materials. For that reason, early DRE test results (i.e., before 1990) should always be treated with caution.

34. In some cases however, operational factors during the testing or sampling and analytical techniques contributed to the low DRE results. These typically were problems that occurred only in the earliest tests conducted during the developmental stages of this technology and should be possible to avoid today. Trial burn is a good way of demonstrating a kilns performance and ability to destroy wastes in an irreversible and sound way, but the design and the conditions of the trial is very crucial.

Early applications of trial burn rules to cement kiln evaluation

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

36. The available reports on cement kilns provides data about performance with regard to the following specific compounds: trichloromethane (chloroform); dichloromethane (methylene chloride); carbon tetrachloride; 1,2-dichloroethane; 1,1,1-trichloroethane; trichloroethylene; tetrachloroethylene; 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113); chlorobenzene; benzene; xylene; toluene ; 1,3,5-trimethylbenzene; methyl

ethyl ketone; methyl isobutyl ketone; carbon hexafluoride; phenoxy acids; chlorinated hydrocarbons; chlorinated aliphatics; chlorinated aromatics; PCBs; and POPs pesticides.

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

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

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

Source: EPA (1986)

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

38. The issue of PIC formation is one about which there is generally great public concern. Some of the kiln tests demonstrated minor increases in PICs resulting from waste combustion. However, tests run on coal-fired facilities demonstrate that PICs are virtually inevitable for these systems. Although trace quantities (<23 parts per trillion) of polychlorinated dibenzodioxins and dibenzofurans were measured at San Juan during a kiln upset, and trace quantities may have been present at Stora Vika, the EPA summary report concludes that they are not confirmed as PICs from waste production.

39. If waste liquid organic chemicals are fed into the firing end of the cement kiln, it can be readily seen that they will be subject to the high temperatures and long residence times of the cement clinker production process. Consequently, they will be completely destroyed by a combination of pyrolysis and oxidation.

Annex 4. Sources of Air Emissions

Particulate Matter

40. The cement production process includes thermal treatment (drying, heating, calcining, clinkerization, cooling) of materials through direct contact with hot gases. It also includes pneumatic material transports and material classification/separation. At the end of these processes, air/gas and pulverized materials have to be separated. Incomplete separation gives rise to dust emissions (kiln/raw mill main stack, clinker cooler stack, cement mill stacks, material transfer point dedusting air outlets).
41. Outdated air pollution control equipment may emit up to several 100 mg/Nm³. EPS easily reach < 50 mg/Nm³. Fabric filters produce values < 20 mg/Nm³. The visibility limit for point source dust is generally assumed to be around 80 mg/Nm³.
42. In the EU, BAT for dust emissions arising from dusty operations other than those from kiln firing, cooling and main milling processes, is to reduce channelled dust emissions from dusty operations (taking into account a maintenance management system) to less than 10 mg/Nm³ (BAT-AEL), as the average over the sampling period (spot measurement, for at least half an hour) by applying dry exhaust gas cleaning with a filter. BAT for dust emissions arising from kiln firing processes is to reduce dust (particulate matter) emissions from flue-gases of kiln firing processes by applying dry exhaust gas cleaning with a filter. The BAT-AEL is <10-20 mg/Nm³, as the daily average value. When applying fabric filters or new or upgraded ESPs, the lower level is achieved. (EIPPCB, 2010)

Sulphur Oxides

43. SO₂ results from the oxidation of sulphide or elemental sulphur contained in the fuel during combustion. In addition, sulphide or elemental sulphur contained in raw materials may be 'roasted' or oxidized to SO₂ in areas of the kiln system where sufficient oxygen is present and the material temperature is in the range of 300-600°C; sulphates in the raw mix can also be converted to SO₂ through localized reducing conditions in the kiln system. The alkaline nature of the cement provides for direct absorption of SO₂ into the product, thereby mitigating the quantity of SO₂ emissions in the exhaust stream.
44. Range of emissions depends on content of volatile sulphur compounds in raw materials: mostly below 300 mg/Nm³; sometimes up to 3000 mg/Nm³.
45. In the EU, BAT for SO_x emissions is to keep the emissions of SO_x low or to reduce the emissions of SO_x from the flue-gases of kiln firing and/or preheating/precalcining processes by applying one of the following measures/techniques: absorbent addition or wet scrubber. (EIPPCB, 2010)
46. BAT associated emission levels for SO_x are (EIPPCB, 2010):

Parameter	Unit	BAT-AEL ¹⁾ (daily average value)
SO _x expressed as SO ₂	mg/Nm ³	<50 – <400

¹⁾ The range takes into account the sulphur content in the raw materials

Moreover, facilities co-processing hazardous and other wastes that are located in the EU have to meet the requirements of the Council Directive 2000/76/EC.

Nitrogen Oxides

47. There are four mechanisms of NO_x formation in cement kilns of which thermal and fuel NO_x formation are the most important. Thermal NO_x results from the oxidation of molecular nitrogen in air at high temperature. This phenomenon occurs in and around the flame in the burning zone of a cement kiln at a temperature greater than 1200°C. Fuel NO_x results from the oxidation of nitrogen in the fuel at any combustion temperature found in the cement process. Because of the lower combustion temperature in the calciner and some sites of supplemental

fuel combustion, the formation of fuel NO_x often exceeds that of thermal NO_x at these locations. The generation of feed NO_x has been demonstrated only in the laboratory by heating nitrogen-containing cement raw materials to the range of 300-800°C in the presence of oxygen. Slow heating, such as occurs in wet and long-dry kilns, appears to increase the yield of NO_x for a given raw material. The yield of feed NO_x is potentially lower when the raw material is heated quickly in a preheater or precalciner system. Prompt NO_x is generated by the reaction of certain fuel-derived radicals with elemental nitrogen in a hydrocarbon flame and is a minor contributor to overall NO_x generation.

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

49. In the EU, BAT for NO_x emissions is to reduce the emissions of NO_x from the flue-gases of kiln firing processes by applying the following measures/techniques individually or in combination (EIPPCB, 2010):

- Primary measures/techniques, such as: flame cooling; low NO_x burners; mid kiln firing; addition of mineralisers to improve the burnability of the raw meal (mineralised clinker); process optimisation;
- Staged combustion (conventional or waste fuels), also in combination with a precalciner and the use of optimised fuel mix;
- SNCR; and
- SCR, subject to appropriate catalyst and process development in the cement industry.

50. BAT associated emission levels for NO_x are (EIPPCB, 2010):

Kiln type	Unit	BAT-AEL (daily average value)
Preheater kilns	mg/Nm^3	<200 – 450 ²⁾
Lepol and long rotary kilns	mg/Nm^3	400 – 800 ¹⁾

¹⁾ Depending on initial levels and ammonia slip
²⁾ BAT-AEL is 500 mg/Nm^3 , where after primary measures/techniques the initial NO_x level is >1000 mg/Nm^3
³⁾ Existing kiln system design, fuel mix properties including waste, raw material burnability can influence the ability to be in the range. Levels below 350 mg/Nm^3 are achieved at kilns with favourable conditions. The lower value of 200 mg/Nm^3 has only been reported as monthly average for three plants (easy burning mix used)

Moreover, facilities co-processing hazardous and other wastes that are located in the EU have to meet the requirements of the Council Directive 2000/76/EC.

Carbon Oxides

51. CO is a PIC of carbonaceous fuels resulting from insufficient oxygen at the combustion site, insufficient mixing of oxygen and fuel at the combustion site, and/or rapid cooling of the combustion products to below the ignition temperature of CO prior to its complete oxidation. CO can be formed unintentionally at any of the combustion sites in the kiln system. The emission of CO usually represents partially burned and under utilized fuel. However, as a result of using oxygen-deficient combustion in the riser duct or calciner as a NO_x control strategy, CO sometimes is generated in the pyroprocess and may appear in the flue gas discharge if it is not somehow oxidized following its formation.

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

Organic Emissions

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

the constituents of petroleum and kerogens found in the raw material mix. The potential for organic emissions varies with the selection of raw materials and the variability of the concentration of organic constituents within raw material sources. Organic PICs also can be formed as a result of incomplete combustion at any of the combustion sites within a pyroprocessing system.

54. Range of emissions is dependant on content of raw materials of volatile organics: mostly below 50 mg/Nm³; sometimes up to 500 mg/Nm³.

55. In the EU, BAT for TOC emissions is to keep the emissions of TOC from the flue-gases of the kiln firing processes low by applying the following measure/technique: avoid feeding raw materials with a high content of volatile organic compounds into the kiln system via the raw material feeding route. In this context, facilities co-processing hazardous and other wastes that are located in the EU have to meet the requirements of the Council Directive 2000/76/EC.

Acid Gases

56. All the oxidants necessary to convert SO₂ to sulphur trioxide (SO₃) are present in the combustion products of fossil fuel. Therefore, emissions of SO₃ and/or H₂SO₄ mist are a possibility from cement plants. The emissions of H₂SO₄ mist may also increase in those plants employing tailpipe wet scrubbers.

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

58. The mechanism for the formation of HCl in cement kilns is not fully understood. Nevertheless, there is limited evidence that HCl emissions may be independent of chlorine input to a kiln system (possibly due to the affinity of chlorine for calcium and alkali metals). Emissions can result if inputs exceed the capacity of the clinker to absorb inbound chlorine.

59. Range of HCl emissions: SP/PC¹¹ kiln systems, <10 mg/Nm³; wet kilns, up to 80 mg/Nm³.

60. In the EU, BAT is to keep the emissions of HCl below 10 mg/Nm³ (BAT-AEL), as the daily average value or average over the sampling period (spot measurements, for at least half an hour), by applying the following primary measures/techniques individually or in combination: using raw materials and fuels containing a low chlorine content, and/or limiting the amount of chlorine content for any waste that is to be used as raw material and/or fuel in a cement kiln. (EIPPCB, 2010)

61. Similarly, BAT is to keep the emissions of HF below 1 mg/Nm³ (BAT-AEL) expressed as HF, as the daily average value or average over the sampling period (spot measurements, for at least half an hour), by applying the following primary measure/technique individually or in combination: using raw materials and fuels containing low fluorine and/or limiting the amount of fluorine content for any waste that is to be used as raw material and/or fuel in a cement kiln. (EIPPCB, 2010)

62. Moreover, facilities co-processing hazardous and other wastes that are located in the EU have to meet the requirements of the Council Directive 2000/76/EC.

Ammonia

63. Trace quantities of NH₃ in the exhaust gas from a cement kiln gas probably result from the pyrolysis of nitrogenous compounds in fossil fuels and raw materials. Ammonia emissions from cement kilns are of primary concern with regard to their potential contribution to regional haze. In addition, atmospheric reactions occur just outside of the stack between NH₃ and the oxides of sulphur or HCl that produce ammonium sulphate, ammonium bisulphate, or ammonium chloride as very fine particulate matter (PM). These reaction products are observed as the undesirable anomaly known as a 'detached plume'. Depending on the location of the stack observer, the detached plume can give the incorrect appearance of poorly controlled PM emissions from a kiln stack.

¹¹ SP = Suspension Preheater kiln; PC = Precalciner kiln

64. Range of emissions is <1 to 15 mg/Nm³ as a rule with exceptions up to 40 mg/Nm³.

Benzene

65. Benzene might be present in conventional and alternative raw materials and is partially roasted off at material preheating.
66. Range of emissions, normally 1 to 2 mg/Nm³; up to 3 and more mg/Nm³ in rare cases

Heavy Metals

67. Heavy metals are ubiquitous in all cement kiln input materials. Since clean gas dust (i.e. dust after the dedusting equipment) is an input materials fraction, it also contains heavy metals. In addition, semi-volatile and volatile heavy metals are evaporated and condense (predominantly) on the fine dust fraction.

68. Most heavy metal emissions remain below the detection limits, and all emissions, except for mercury, remain safely below generally adopted limit values. Mercury emissions can exceed limit values (0.05 mg/Nm³ for the European Union) in case of excessive inputs with materials.

69. In the EU, BAT for metal emissions is to minimise the emissions of metals from the flue-gases of the kiln firing processes by applying the following measures/techniques individually or in combination (EIPPCB, 2010):

- Selecting materials with a low content of relevant metals and limiting the content of relevant metals in materials, especially mercury;
- Using a quality assurance system to guarantee the characteristics of the waste materials used; and
- Using effective dust removal measures/techniques.

70. BAT associated emission levels for metal emissions are (EIPPCB, 2010):

Metals	Unit	BAT-AEL (average over the sampling period (spot measurements, for at least half an hour))
Fe	mg/Nm ³	<0.05 ¹⁾
T (Cd, Tl)	mg/Nm ³	<0.05 ¹⁾
T (As, Sb, Pb, Cr, Co, Cu, Mn, Ni, V)	mg/Nm ³	<0.5 ¹⁾
¹⁾ Low levels have been reported, see Sections 1.3.4.7, 1.3.4.7.1 and 1.4.7 ²⁾ Low levels have been reported (see Sections 1.3.4.7, 1.3.4.7.1 and 1.4.7). Values higher than 0.03 mg/Nm ³ have to be further investigated. Values close to 0.05 mg/Nm ³ require consideration of additional measures/techniques such as those described in Sections 1.3.4.13, 1.3.9.1 and 1.4.7		

71. In the above context, facilities co-processing hazardous and other wastes that are located in the EU have to meet the requirements of the Council Directive 2000/76/EC.

Polychlorinated Dibenzop-dioxins and Polychlorinated Dibenzofurans

72. Dioxins, furans or advanced precursors might be present in conventional (rarely) and alternative raw materials and are partially roasted off at material preheating. Any chlorine input in the presence of organic material may potentially cause the formation of PCDD and PCDF in heat (combustion) processes. PCDD/PCDF can be formed by the de novo synthesis mechanism in or after the preheater and in the air pollution control device if chlorine and hydrocarbon precursors are available in sufficient quantities in the temperature range 200° C to 450° C.

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

74. In a survey performed by CEMBUREAU, PCDD and PCDF measurements from 110 cement kilns in 10 countries were presented. The countries covered by the survey were Czech Republic, Denmark, France, Germany, Hungary, Italy, the Netherlands, Norway, Spain and the United Kingdom. The average concentration,

taking into account all of the data in this dataset, was 0.016 ng I-TEQ/m³. The range between the lowest and highest concentrations measured was < 0.001 to 0.163 ng I-TEQ/m³. All measurements were expressed corrected to standard conditions (dry gas, 273 K, 101.3 kPa and 10% O₂).

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

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

- Most cement kilns can meet an emission level of 0.1 ng TEQ/Nm³ if primary measures are applied;
- Co-processing of AFR, fed to the main burner, kiln inlet or the precalciner does not seem to influence or change the emissions of POPs;
- Data from dry preheater and precalciner cement kilns in developing countries show emission levels much lower than 0.1 ng TEQ/Nm³.

77. In the EU, BAT is to avoid emissions of PCDDs/PCDFs or to keep the emissions of PCDDs/PCDFs from the flue-gases of the kiln firing processes low by applying the following measures/techniques individually or in combination (EIPPCB, 2010):

- Carefully selecting and controlling of kiln inputs (raw materials), i.e. chlorine, copper and volatile organic compounds;
- Carefully selecting and controlling of kiln inputs (fuels), i.e. chlorine and copper;
- Limiting/avoiding the use of wastes which contain chlorinated organic materials;
- Avoid feeding fuels with a high content of halogens (e.g. chlorine) in secondary firing;
- Quick cooling of kiln exhaust gases to lower than 200 °C and minimising residence time of flue-gases and oxygen content in zones where the temperatures range between 300 and 450 °C; and/or
- Stop feeding waste for operations such as start-ups and/or shutdowns.

78. The BAT-AELs are <0.05-0.1 ng PCDD/F I-TEQ/Nm³, as the average over the sampling period (6 – 8 hours) (EIPPCB, 2010). Furthermore, facilities co-processing hazardous and other wastes that are located in the EU shall need to meet the requirements of the Council Directive 2000/76/EC.

Polychlorinated Biphenyls and Hexachlorobenzene

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

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

Annex 5. Examples of Emission Limit Values for Cement Kilns Co-processing Hazardous Waste

Republic of Chile (Source: Supreme Decree N°45, 5 March 2007)

Pollutant	Total emission limit values (a)
Dioxins and furans	0.2 ng TEQ/Nm ³
Particulate matter	50 mg/Nm ³
Mercury and compounds (Hg)	0.1 mg/Nm ³
Cadmium and compounds (Cd)	0.1 mg/Nm ³
Beryllium and compounds (Be)	0.1 mg/Nm ³
Lead and compounds (Pb)	1 mg/Nm ³
Arsenic, cobalt, nickel, selenium and tellurium, and compounds (As + Co + Ni + Se + Te)	1 mg/Nm ³
Antimony, chromium, manganese and vanadium, and compounds (Sb + Cr + Mn + V)	5 mg/Nm ³
Hydrogen chloride (HCl)	20 mg/Nm ³
Hydrogen fluoride (HF)	2 mg/Nm ³
Benzene	5 mg/Nm ³
Total organic carbon (TOC)	20 mg/Nm ³ (b)

(a) Values corrected to 10% oxygen, at normal conditions of 101 kPa 298K/ 25°C.

(b) Exemptions may be authorised by the competent authority in cases where TOC does not result from the burning of waste.

Republic of South Africa (Source: National Policy on Thermal Treatment of General and Hazardous Waste, Government Gazette (Staatskoerant), 24 July 2009)

Emissions	Air emission standard (a)
PM (Total particulate matter)	30 (b) - 80 (c)
TOC	10 (d)
HCl	10
HF	1
SO ₂	50 (d)
NO _x	500 (e)
Hg	0,05
Cd, Tl (Sum total)	0,05
Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V (Sum total)	0,5
PCDD/PCDF (ng/Nm ³ 1-TEQ)	0,1

(a) Concentration expressed as mg/Nm³ (daily average) unless otherwise stated, and at normalized conditions of 10% O₂, 101,3 kPa 273K/ 0°C, dry gas.

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

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

(d) Limits for TOC or SO₂ do not apply where elevated emissions result from conventional fuels or raw material, i.e. not from the co-processing of AFR provided that current TOC and SO₂ emissions (as established through baseline monitoring) are not exceeded the introduction of AFR.

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

European Union (Source: Directive 2000/76/EC of the European Parliament and of the Council)

Pollutant	Total emission limit values (a) (b)
Dioxins and furans	0.1 ng TEQ/m ³
Total dust	30 mg/m ³
Mercury (Hg)	0.05 mg/m ³
Cadmium and thallium (Cd + Tl)	0.05 mg/m ³
Antimony, arsenic, lead, chromium, cobalt, copper, manganese, nickel and vanadium (Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V)	0.5 mg/m ³
Carbon monoxide (CO)	(c)
Hydrogen chloride (HCl)	10 mg/m ³
Hydrogen fluoride (HF)	1 mg/m ³
Oxides of nitrogen (NO _x)	
– existing plants (c)	800 mg/m ³
– new plants	500 mg/m ³
Sulfur dioxide (SO ₂)	50 mg/m ³ (d)
Total organic carbon (TOC)	10 mg/m ³ (d)

(a) Values corrected to 10% oxygen, dry basis.

(b) If in a co-incineration plant more than 40 % of the resulting heat release comes from hazardous waste, the emission limit values set out in Annex V shall apply.

(c) Emission limit values for CO can be set by the competent authority.

(d) Exemptions may be authorised by the competent authority in cases where TOC and SO₂ does not result from the incineration of waste.

(e) Existing co-incineration plant means a plant:

- Which is in operation and has a permit in accordance with existing Community legislation before 28 December 2002, or,
- Which is authorised or registered for incineration or co-incineration and has a permit issued before 28 December 2002 in accordance with existing Community legislation, provided that the plant is put into operation not later than 28 December 2003, or
- Which, in the view of the competent authority, is the subject of a full request for a permit, before 28 December 2002, provided that the plant is put into operation not later than 28 December 2004.

United States (Source: 40CFR63 Subpart EEE, "Replacement standards")

Pollutant	Emission and hazardous waste feed limits for kilns that were constructed or reconstructed after April 20, 2004 (a) (b)	Emission and hazardous waste feed limits for kilns that were constructed or reconstructed before April 20, 2004 (a) (b)
Dioxin/Furans	(i) 0.20 ng TEQ/dscm; <u>or</u> (ii) 0.40 ng TEQ/dscm provided that the combustion gas temperature at the inlet to the initial dry particulate matter control device is 400 °F or lower	(i) 0.20 ng TEQ/m ³ ; <u>or</u> (ii) 0.40 ng TEQ/m ³ (provided that the combustion gas temperature at the inlet to the initial dry particulate matter control device is 400 °F or lower)
Particulate matter	(i) 0.0069 gr/ft ³ ; <u>and</u> (ii) Opacity greater than 20 percent (does not apply to a sources equipped with a bag leak detection system under 40CFR63.1206(c)(8) or a particulate matter detection system under 40CFR63.1206(c)(9)) ¹²	(i) 0.028 gr/ft ³ ; <u>and</u> (ii) Opacity greater than 20 percent (does not apply to a sources equipped with a bag leak detection system under 40CFR63.1206(c)(8) or a particulate matter detection system under 40CFR63.1206(c)(9)) <i>(Particulate matter as a surrogate for antimony, cobalt, manganese, nickel, and selenium)</i>
Mercury (c)	(i) 1.9 ppmw (average as-fired concentration of mercury in all hazardous waste feedstreams); <u>and</u> (ii) <u>Either</u> : (A) 120 µg/m ³ <u>or</u> (B) 120 µg/m ³ (hazardous waste feed maximum theoretical emission concentration (MTEC))	(i) 3.0 ppmw (average as-fired concentration of mercury in all hazardous waste feedstreams); <u>and</u> (ii) <u>Either</u> : (A) 120 µg/m ³ <u>or</u> (B) 120 µg/m ³ (hazardous waste feed maximum theoretical emission concentration (MTEC ¹³))
Semivolatile metals (Pb + Cd)	(i) 6.2×10 ⁻⁵ lbs/10 ⁶ Btu (mass of pollutant attributable to the hazardous waste per million Btu heat input from the hazardous waste); <u>and</u> (ii) 180 µg/m ³ (*)	(i) 7.6×10 ⁻⁴ lbs/10 ⁶ Btu (mass of pollutant attributable to the hazardous waste per million Btu heat input from the hazardous waste); <u>and</u> (ii) 330 µg/m ³ (*)
Low volatile metals (As + Be + Cr)	(i) 1.5×10 ⁻⁵ lbs/10 ⁶ Btu (mass of pollutant attributable to the hazardous waste per million Btu heat input from the hazardous waste); <u>and</u> (ii) 54 µg/m ³ (*)	(i) 2.1×10 ⁻⁵ lbs/10 ⁶ Btu (mass of pollutant attributable to the hazardous waste per million Btu heat input from the hazardous waste); <u>and</u> (ii) 56 µg/m ³ (*)

¹² Federal Register, October 28, 2008 (Volume 73, Number 209), National Emission Standards for Hazardous Air Pollutants: Standards for Hazardous Waste Combustors: Reconsideration

¹³ MTEC is defined as the metals feedrate divided by the gas flow rate and is expressed in units of ug/m³.

Pollutant	Emission and hazardous waste feed limits for kilns that were constructed or reconstructed after April 20, 2004 (a) (b)	Emission and hazardous waste feed limits for kilns that were constructed or reconstructed before April 20, 2004 (a) (b)
Carbon monoxide (CO) or hydrocarbons (HC)	<p>– Cement kilns equipped with a by-pass duct or midkiln gas sampling system:</p> <p>(i) HC and CO in the by-pass or midkiln gas sampling system: (A)(a) 100 ppmv CO, <u>and</u> (b) 10 ppmv HC (as propane) during DRE test runs; <u>or</u> (B) 10 ppmv HC (as propane)</p> <p>(ii) HC and CO in the main stack: 50 ppmv HC (as propane) (kilns whose construction commenced after April 19, 1996 at a plant site where a cement kiln (whether burning hazardous waste or not) did not previously exist)</p> <p>– Cement kilns not equipped with a bypass duct or midkiln gas sampling system (HC and CO in the main stack): (A) 20 ppmv HC (as propane); <u>or</u> (B)(a) 100 ppmv CO, <u>and</u> (b) 20 ppmv HC (as propane) during DRE test runs</p>	<p>– Cement kilns equipped with a by-pass duct or midkiln gas sampling system (HC and CO in the by-pass duct or mid-kiln gas sampling system): (A)(a) 100 ppmv CO, <u>and</u> (b) 10 ppmv HC (as propane) during DRE test runs; <u>or</u> (B) 10 ppmv HC (as propane)</p> <p>– Cement kilns not equipped with a bypass duct or midkiln gas sampling system (HC and CO in the main stack): (A) 20 ppmv HC (as propane); <u>or</u> (B)(a) 100 ppmv CO, <u>and</u> (b) 20 ppmv HC (as propane) during DRE test runs <i>(Carbon monoxide/ total hydrocarbons as surrogates for non-dioxin organic hazardous air pollutants (HAP))</i></p>
Total chlorine (HCl + Cl ₂) (*)	86 ppmv (as chloride) (sources may establish and comply with health-based compliance alternatives for total chlorine under the procedures prescribed in 40CFR63.1215)	120 ppmv (as chloride) (sources may establish and comply with health-based compliance alternatives for total chlorine under the procedures prescribed in 40CFR63.1215)
Destruction and removal efficiency (DRE)	<p>(i) 99.99% DRE (for each principle organic hazardous constituent (POHC)): DRE = $[1 - (W_{out}/W_{in})] \times 100\%$ W_{in} = mass feedrate of one principal organic hazardous constituent (POHC) in a waste feedstream; and W_{out} = mass emission rate of the same POHC present in exhaust emissions prior to release to the atmosphere.</p> <p>(ii) 99.9999% DRE (for dioxin-listed hazardous wastes) (DRE performance must be demonstrated on POHCs that are more difficult to incinerate than tetra-, penta-, and hexachlorodibenzo-p-dioxins and dibenzofurans)</p>	<p>(i) 99.99% DRE (for each principle organic hazardous constituent (POHC14)): DRE = $[1 - (W_{out}/W_{in})] \times 100\%$ W_{in} = mass feedrate of one principal organic hazardous constituent (POHC) in a waste feedstream; and W_{out} = mass emission rate of the same POHC present in exhaust emissions prior to release to the atmosphere.</p> <p>(ii) 99.9999% DRE (for dioxin-listed hazardous wastes) (DRE performance must be demonstrated on POHCs that are more difficult to incinerate than tetra-, penta-, and hexachlorodibenzo-p-dioxins and dibenzofurans)</p>

¹⁴ One or more POHCs must be specified that are representative of the most difficult to destroy organic compounds in the hazardous waste feedstream. This specification must be based on the degree of difficulty of incineration of the organic constituents in the hazardous waste and on their concentration or mass in the hazardous waste feed, considering the results of hazardous waste analyses or other data and information.



(a) Values corrected to 7% oxygen, dry basis.

(b) The following hazardous wastes are not subject to regulation under 40CFR63 Subpart EEE:

- A. A conditionally exempt small quantity generator's hazardous wastes
- B. Used oil burned for energy recovery that is also a hazardous waste solely because it exhibits a hazardous characteristic (ignitability, reactivity, corrosivity, toxicity)
- C. Comparable fuels or comparable syngas fuels (i.e., comparable/syngas fuels) that meet the requirements of 40CFR261.38:
 - a. Comparable fuel specifications:
 - (1) Physical specifications:
 - (i) The heating value must exceed 5,000 BTU/lb (11,500 J/g)
 - (ii) The viscosity must not exceed 50 cs, as-fired.
 - (2) Constituent specifications: See Table 1 of section 40CFR261.38
 - b. Synthesis gas fuel (i.e. syngas fuel) that is generated from hazardous waste must:
 - (1) Have a minimum Btu value of 100 Btu/Scf;
 - (2) Contain less than 1 ppmv of total halogen;
 - (3) Contain less than 300 ppmv of total nitrogen other than N₂;
 - (4) Contain less than 200 ppmv of HS; and
 - (5) Contain less than 1 ppmv of each hazardous constituent in the target list of Appendix VIII constituents of 40CFR261

(c) Alternative standards may be petitioned under section 63.1206(b)(10), if (A) the source cannot achieve one or more of these standards while using maximum achievable control technology (MACT) because of raw material contributions to emissions of mercury, semivolatile metals, low volatile metals, or hydrogen chloride/chlorine gas; or (B) mercury is not present at detectable levels in the raw material. However, EPA currently intends to seek a remand of these alternative metals and total chlorine standards and remove these provisions in a subsequent rulemaking¹⁵.

¹⁵ Federal Register, September 27, 2007 (Volume 72, Number 187), NESHAP: National Emission Standards for Hazardous Air Pollutants: Standards for Hazardous Waste Combustors: Proposed Rules



ANEXO 2

EU Submission to Chile and the Basel Secretariat on the Draft Technical Guidelines On Co-Processing Of Hazardous Waste In Cement Kilns

30 August 2010