ANNEX 1
Clinker Production Process
ANNEX 1 - CLINKER PRODUCTION PROCESS

A. Introduction

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 per cent 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.

B. 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 1A, 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’ constituents 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.

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1 Sometimes called “accessory” or “sweetener” materials (van Oss, 2005).
Table 1A - Chemical composition of ordinary Portland cement clinker and conventional raw materials

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Clinker</th>
<th>Limestone, lime marl, chalk</th>
<th>Clay</th>
<th>Sand</th>
<th>Iron ore</th>
<th>Bauxite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.71-24.25%</td>
<td>0.5-50%</td>
<td>33-78%</td>
<td>80-99%</td>
<td>4-11%</td>
<td>2.9%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.76-6.78%</td>
<td>0.1-20%</td>
<td>7-30%</td>
<td>0.5-7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.21-0.52%</td>
<td>0.0-0.7%</td>
<td>0.2-1.8%</td>
<td>0.0-0.5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ + TiO₂</td>
<td></td>
<td></td>
<td>7-30%</td>
<td>0.5-2%</td>
<td>0.2-3%</td>
<td>57.5%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.29-4.64%</td>
<td>0.2-5.9%</td>
<td>4.0-15%</td>
<td>0.0-4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.03-0.68%</td>
<td>0.02-0.15%</td>
<td>0.09%</td>
<td>0.051%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃ + Mn₂O₃</td>
<td></td>
<td></td>
<td>0.1-10%</td>
<td>2-15%</td>
<td>0.5-2%</td>
<td>19-95%</td>
</tr>
<tr>
<td>CaO</td>
<td>63.76-70.14%</td>
<td>20-55%</td>
<td>0.2-25%</td>
<td>0.1-3%</td>
<td>0.1-34%</td>
<td>2.4%</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00-4.51%</td>
<td>0.2-6%</td>
<td>0.3-5%</td>
<td>0.3-0.5%</td>
<td>≤1.5%</td>
<td>0.04%</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.31-1.76%</td>
<td>0.3-5%</td>
<td>0.4-5%</td>
<td>0.2-3%</td>
<td>Traces</td>
<td>0.04%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.03-0.335</td>
<td>0.0-1.5%</td>
<td>0.1-1.5%</td>
<td>0.0-1%</td>
<td>Traces</td>
<td>0.02%</td>
</tr>
<tr>
<td>Cl</td>
<td></td>
<td></td>
<td>0.0-0.6%</td>
<td>0.0-1%</td>
<td>Traces</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.02-0.27%</td>
<td>0.0-0.8%</td>
<td>0.0-1.0%</td>
<td>0.0-0.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loss on ignition (CO₂ + H₂O)</td>
<td>0.09-1.56%</td>
<td>2-44%</td>
<td>1-20%</td>
<td>≤5</td>
<td>0.1-30%</td>
<td>13.5%</td>
</tr>
</tbody>
</table>

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 rapidly². 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 1B.

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, 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 over stressing 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. The typical concentration of trace elements in the primary fuels is as in Table 1C. 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

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² Such clinker used to make concrete can cause destructive expansion of hardened concrete through slow reaction with water.
with calcium and potassium, causing operational problems in the cool end of the
kiln. Halogens are of concern because chlorides can cause operational problems
similar to those caused by sulphur. Chlorine concentrations in coal can range from
100 to 2800 parts per million. (U.S. EPA, 1993)

12. Both heat and electricity consumption vary significantly with kiln technology as
presented in Table 1D and, for the same general technology, plants operating
multiple kilns tend to have higher energy requirement per tonne of overall output
capacity than the plants with the same overall capacity that operate a single kiln.
Wet kilns consume more fuel on a unit basis than the 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>
<thead>
<tr>
<th>Constituent</th>
<th>Limestone Min-Max (AV)</th>
<th>Marl Min-Max (AV)</th>
<th>Clay Min-Max (AV)</th>
<th>Sand Min-Max (AV)</th>
<th>Iron ore Min-Max (AV)</th>
<th>Gypsum/anhydrite Min-Max (AV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.1-15 (3)</td>
<td>0.2-12 (0)</td>
<td>2-100 (14)</td>
<td>0.4-42 (11)</td>
<td>2-1200 (37)</td>
<td>0.2-3.5 (1.5)</td>
</tr>
<tr>
<td>Be</td>
<td>0.01-12 (0.3)</td>
<td>n.a.-1 (0.5)</td>
<td>1-7 (3)</td>
<td>0.6-1.5 (1.0)</td>
<td>0.8-2 (1)</td>
<td>0.02-0.9 (0.2)</td>
</tr>
<tr>
<td>Cd</td>
<td>0.02-2 (0.2)</td>
<td>0.02-0.5 (0.3)</td>
<td>0.01-1 (0.2)</td>
<td>0.01-1 (0.2)</td>
<td>0.02-15 (6)</td>
<td>0.03-2.3 (0.15)</td>
</tr>
<tr>
<td>Co</td>
<td>0.1-7 (3)</td>
<td>n.a.-28 (5)</td>
<td>6-25 (20)</td>
<td>0.3-37 (11)</td>
<td>109-183 (144)</td>
<td>0.02-3.9 (1)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.5-184 (14)</td>
<td>1.2-71 (28)</td>
<td>15-260 (85)</td>
<td>1-220 (19)</td>
<td>8-1400 (495)</td>
<td>1-27.3 (8.8)</td>
</tr>
<tr>
<td>Cu</td>
<td>5-57 (11)</td>
<td>4.9-35 (12)</td>
<td>10-285 (43)</td>
<td>1.2-85 (10)</td>
<td>(1520)</td>
<td>0.3-12.8 (7)</td>
</tr>
<tr>
<td>Hg</td>
<td>0.005-0.1 (0.04)</td>
<td>0.005-0.1 (0.03)</td>
<td>0.01-0.5 (0.2)</td>
<td>0.01-1 (0.02)</td>
<td>n.a.-1 (0.5)</td>
<td>0.00625-1.3 (0.1)</td>
</tr>
<tr>
<td>Mn</td>
<td>250-3300 (500)</td>
<td>n.a.-3300 (360)</td>
<td>n.a.-2500 (600)</td>
<td>46-2040 (194)</td>
<td>900-1200 (1090)</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ni</td>
<td>1.4-131 (16)</td>
<td>1.5-57 (16)</td>
<td>7-236 (83)</td>
<td>1-73 (13)</td>
<td>5-815 (331)</td>
<td>0.3-14.5 (5.5)</td>
</tr>
<tr>
<td>Pb</td>
<td>0.27-151 (18)</td>
<td>0.3-57 (12)</td>
<td>1-219(25)</td>
<td>0.7-70 (10)</td>
<td>4-8700 (350)</td>
<td>0.2-20.5 (7)</td>
</tr>
<tr>
<td>Element</td>
<td>0.2-27 (1)</td>
<td>n.a.-27 (4)</td>
<td>0.5-13 (2)</td>
<td>0.3-12 (7)</td>
<td>(26)</td>
<td>0.1-5 (1)</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td>-----------</td>
<td>------</td>
<td>----------</td>
</tr>
<tr>
<td>Sb</td>
<td>0.4-30 (0.6)</td>
<td>n.a. (1)</td>
<td>n.a.-2.5 (0.5)</td>
<td>n.a. (1)</td>
<td>(8)</td>
<td>0.6-17 (0.8)</td>
</tr>
<tr>
<td>Se</td>
<td>0.9-24 (4)</td>
<td>n.a.-24 (3)</td>
<td>1.6-30 (5)</td>
<td>1.8-40 (3)</td>
<td>n.a.-500 (25)</td>
<td>n.a.</td>
</tr>
<tr>
<td>Sn</td>
<td>n.a. (0.7)</td>
<td>n.a. (1)</td>
<td>n.a. (0.5)</td>
<td>n.a. (0.5)</td>
<td>n.a.-13 (10)</td>
<td>n.a.</td>
</tr>
<tr>
<td>Te</td>
<td>0.05-3 (0.3)</td>
<td>0.05-0.68 (0.6)</td>
<td>0.1-1.6 (0.5)</td>
<td>0.05-1 (0.2)</td>
<td>0.1-400 (2)</td>
<td>0.1-1.0 (0.3)</td>
</tr>
<tr>
<td>Ti</td>
<td>5-80 (26)</td>
<td>n.a.-49 (20)</td>
<td>30-500 (130)</td>
<td>2-240 (50)</td>
<td>10-690 (256)</td>
<td>1-27.8 (13.5)</td>
</tr>
<tr>
<td>V</td>
<td>0.1-229 (30)</td>
<td>22-79 (48)</td>
<td>2-304 (78)</td>
<td>4.2-112 (25)</td>
<td>24-9400 (3288)</td>
<td>1-59 (19)</td>
</tr>
<tr>
<td>Zn</td>
<td>n.a. (5.9)</td>
<td>n.a.</td>
<td>1-58</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Br /f/</td>
<td>50-240 n.a.</td>
<td>15-450 n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Cl /f/</td>
<td>100-940 n.a.</td>
<td>300-990 n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>F /f/</td>
<td>0.25-0.75 n.a.</td>
<td>0.2-2.2 n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

/ Source: Aichhorn & others (2003), unless otherwise noted. 
/ Matus (1992)
Table 1C - Trace element concentrations (in parts per million) in primary fuels
(Min = minimum value; Max = maximum value; n.a. = no data available)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Anthracite Min-Max</th>
<th>Bituminous coal Min-Max</th>
<th>Lignite Min-Max</th>
<th>Petroleum coke Min-Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>1-200</td>
<td>n.a.</td>
<td>0.1-12</td>
<td>0.2-0.8</td>
</tr>
<tr>
<td>Be</td>
<td>0-8</td>
<td>n.a.</td>
<td>0.04-0.6</td>
<td>0.02-0.03</td>
</tr>
<tr>
<td>Cd</td>
<td>0.01-10</td>
<td>n.a.</td>
<td>0.06-2.4</td>
<td>0.04-4</td>
</tr>
<tr>
<td>Co</td>
<td>0.5-43</td>
<td>n.a.</td>
<td>0.5-4.2</td>
<td>n.a.</td>
</tr>
<tr>
<td>Cr</td>
<td>1-260</td>
<td>n.a.</td>
<td>0.9-20</td>
<td>0.9-104</td>
</tr>
<tr>
<td>Cu</td>
<td>0.30-60</td>
<td>n.a.</td>
<td>0.4-15</td>
<td>n.a.</td>
</tr>
<tr>
<td>Hg</td>
<td>0.01-3</td>
<td>n.a.</td>
<td>0.01-0.7</td>
<td>0.01-0.09</td>
</tr>
<tr>
<td>Mn</td>
<td>5-356</td>
<td>n.a.</td>
<td>50-160</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ni</td>
<td>1-110</td>
<td>n.a.</td>
<td>0.6-29</td>
<td>24-355</td>
</tr>
<tr>
<td>Pb</td>
<td>5-270</td>
<td>n.a.</td>
<td>0.7-34</td>
<td>1-102</td>
</tr>
<tr>
<td>Sb</td>
<td>0.05-5</td>
<td>n.a.</td>
<td>0.04-2.5</td>
<td>n.a.</td>
</tr>
<tr>
<td>Se</td>
<td>0-6</td>
<td>n.a.</td>
<td>0.4-25</td>
<td>n.a.</td>
</tr>
<tr>
<td>Sn</td>
<td>1.3-7.8</td>
<td>n.a.</td>
<td>0.5-15</td>
<td>n.a.</td>
</tr>
<tr>
<td>Te</td>
<td>0.2-5.0</td>
<td>n.a.</td>
<td>0.1-10</td>
<td>n.a.</td>
</tr>
<tr>
<td>Tl</td>
<td>0.1-5</td>
<td>n.a.</td>
<td>0.05-0.4</td>
<td>0.04-3.1</td>
</tr>
<tr>
<td>V</td>
<td>10-250</td>
<td>n.a.</td>
<td>0.1-84</td>
<td>45-1435</td>
</tr>
<tr>
<td>Zn</td>
<td>4.5-405</td>
<td>n.a.</td>
<td>1-70</td>
<td>16-220</td>
</tr>
<tr>
<td>Br a/</td>
<td>n.a.</td>
<td>7-11</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Cl a/</td>
<td>n.a.</td>
<td>100-2800</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>F a/</td>
<td>n.a.</td>
<td>50-370</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>I a/</td>
<td>n.a.</td>
<td>0.8-11.2</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

a/ Mantus (1992)
Source: Achternbosch et al. (2003), unless otherwise noted.
Table 1D - Energy requirements for clinker manufacture

<table>
<thead>
<tr>
<th>Process</th>
<th>Fuel consumption, GJ/tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical shaft kiln</td>
<td>3.7-6.6</td>
</tr>
<tr>
<td>Wet process</td>
<td>5.9-6.7</td>
</tr>
<tr>
<td>Long dry process</td>
<td>4.6</td>
</tr>
<tr>
<td>1 stage cyclone preheater</td>
<td>4.2</td>
</tr>
<tr>
<td>2 stage cyclone preheater</td>
<td>3.8</td>
</tr>
<tr>
<td>4 stage cyclone preheater</td>
<td>3.3</td>
</tr>
<tr>
<td>4 stage preheater + precal ciner</td>
<td>3.1</td>
</tr>
<tr>
<td>5 stage preheater + precal ciner</td>
<td>3.0-3.1</td>
</tr>
<tr>
<td>6 stage preheater + precal ciner</td>
<td>2.9</td>
</tr>
</tbody>
</table>


C. Manufacturing process

13. Portland cement production begins with the manufacture of clinker followed by its fine grinding with gypsum and other additives to make the finished cement product. Grinding can occur on site or at offsite grinding plants known as cement mills. Clinker manufacture involves the quarrying, crushing, and proportioning of raw materials to produce either a raw meal for the dry and semi-dry processes or a slurry for the wet and semi-wet processes. Once the material is prepared, the raw mix is fed into a kiln where it is heated as it moves through a number of chemical and physical processes necessary for forming 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 1A.

15. The first drying and preheating zone, occurs in a temperature range of from <100 to 750°C. Here, residual or free water is evaporated from the raw meal feed, the clay materials begin to decompose and the bound water is removed so that they become dehydrated. Next is the calcining zone, where materials temperatures range from 750 to 1000°C. The material is 'calcined', where the calcium carbonate (CaCO₃) in the limestone is dissociated producing calcium oxide (CaO, lime) and liberating carbon dioxide (CO₂) gas. 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 as C₂S, C₃S, C₃A, and C₄AF 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.

**Figure 1A - Diagram of ‘reaction’ zones for different kiln technologies**

Source: van Oss (2005)

16. In the clinker burning process, it is essential to maintain kiln charge temperatures in the sintering zone between 1400 and 1500°C to convert the raw meal to clinker. To reach these temperatures, flame temperatures of about 2000°C are necessary. Also, for reasons of clinker quality, excess air is required in the sintering zone to maintain oxidizing conditions. Otherwise, if insufficient oxygen is present, tetracalcium alumino ferrite does not form; instead Fe₂O₃ 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)

17. The composition of the clinker, as well as the names and formulas of the clinker components are listed in Table 1E.

18. To complete the production of Portland cement, the cooled clinker is ground with a small amount of gypsum or anhydrite. **Figure 1** in the main Guidelines and **Figure 1B** provides a process flow diagram of the general cement manufacturing process.
Table 1E - Typical mineralogical composition of ordinary Portland cement clinker

<table>
<thead>
<tr>
<th>Chemical name (common name)</th>
<th>Chemical formula</th>
<th>Common notation a/</th>
<th>Concentration range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate ('alite')</td>
<td>Ca$_3$SiO$_5$</td>
<td>C$_3$S</td>
<td>50-70%</td>
</tr>
<tr>
<td>Dicalcium silicate ('belle')</td>
<td>Ca$_2$SiO$_4$</td>
<td>C$_2$S</td>
<td>15-30%</td>
</tr>
<tr>
<td>Tricalcium aluminate ('aluminate')</td>
<td>Ca$_3$Al$_2$O$_6$</td>
<td>C$_3$A</td>
<td>5-10%</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite ('ferrite')</td>
<td>Ca$_4$Al$_2$Fe$<em>2$O$</em>{10}$</td>
<td>C$_4$AF</td>
<td>5-15%</td>
</tr>
</tbody>
</table>

a/ Abbreviations: C=CaO; S=SiO$_2$; A=Al$_2$O$_3$; F=Fe$_2$O$_3$
Source: Taylor (1997)

19. 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; Höne 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):

(a) **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.

(b) **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.

(c) **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.

(d) **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).
Figure 1B: General overview of a cement manufacturing process
Source: CEMBUREAU (2006)
20. In China, approximately 60% of the cement was produced in 2005 in VSKs, an amount that is expected to drop to 50% by 2015 (Karstenensen, 2006a). In Europe, about 90% of the cement production is from dry process kilns, a further 7.5% of production is accounted for by semi-dry and semi-wet process kilns, with the remainder of European production, about 2.5 per cent, coming from wet process kilns (EIPPCB, 2010). In the United States, no new wet kilns have been built since 1975, and approximately 80% of U.S. cement production capacity now relies on the dry process technology (U.S. EPA, 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 1F provides the share mix of kiln technologies in each region or country in 2002.

Table 1F - Share of different kiln types in 2002

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

Source: Baron et al. (2007)

21. 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 (Karstenensen, 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.
ANNEX 2

QUALITY ASSURANCE AND QUALITY CONTROL PROGRAM IN THE IMPLEMENTATION OF CO-PROCESSING IN CEMENT PLANT
ANNEX 2 – QUALITY ASSURANCE AND QUALITY CONTROL PROGRAM IN THE IMPLEMENTATION OF CO-PROCESSING IN CEMENT PLANT

1. A comprehensive programme for quality assurance (QA) and quality control (QC) should be applied. The aim is to ensure that the product meets standard specifications, plant operations are not negatively affected by the use of hazardous wastes, environmental protection and to reduce health and safety risks. QA is necessary for ensuring that all data and the decisions resulting from that data are technically sound, statistically valid, and properly documented.

2. A QA plan should be prepared to help ensure that the monitoring, sampling, and analytical data meet specific objectives for precision, accuracy, and completeness and to provide the framework for evaluating data quality. The plan should cover waste streams and product materials handled at the facility with detailed instructions for the following:

   (a) Organization and responsibilities;
   (b) QA objectives for data measurement of precision, accuracy, completeness, representativeness, and comparability;
   (c) Sampling procedures;
   (d) Sample handling and custody;
   (e) Analytical procedures;
   (f) QC checks (blanks, spikes, replicates, etc.) and frequency;
   (g) Instrument/equipment testing, inspection, or maintenance;
   (h) Instrument/equipment calibration procedures and frequency;
   (i) Data review, verification, validation, and reporting.

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

4. Safety and health should be taken into consideration when conducting sampling. Employees carrying out sampling require training for the hazards associated with waste, handling procedures, protective clothing and equipment. Those involved in sampling activities should be fully aware of applicable QA/QC procedures.

5. BAT for waste quality control in cement manufacturing processes is outlined by the EIPPCB (2010):

   (a) To apply QA systems to guarantee the characteristics of wastes and to analyse any waste that is to be used as raw material and/or fuel in a cement kiln for: maintenance of quality over time; physical criteria, for example, emissions formation, coarseness, reactivity, burnability, calorific value; chemical criteria, for example, chlorine, sulphur, alkali and phosphate content and relevant metals content;
(b) To control the amount of relevant parameters for any waste that is to be used as raw material and/or fuel in a cement kiln, such as chlorine, relevant metals (for example, cadmium, mercury, thallium), sulphur, total halogen content;
(c) To apply QA systems for each waste load.

6. Internal audits should be carried out with a frequency that ensures QA/QC procedures are in use and that personnel conform to them. Independent third party audits should be conducted at least annually or as required to determine the effectiveness of the implemented quality system. Audit reports should be submitted to management with requirements to correct observed deficiencies.
ANNEX 3

HEALTH AND SAFETY ASPECTS
ANNEX 3 – HEALTH AND SAFETY ASPECTS

1. Health and safety should be a conscious priority and integrated into all aspects of operations during hazardous waste management. Overall and specific personnel requirements, the chain of command, and individual roles and responsibilities, should be clearly established.

2. A health and safety programme should be designed to identify, evaluate, and control safety and health hazards, and provide for emergency response for hazardous waste operations. The content and extent of this programme should be proportionate to the types and degrees of hazards and risks associated with specific operations.

3. Adequate documentation and information on safe hazardous waste handling, operating procedures and contingency measures should be available. Through openness and transparency, facility management should ensure the workforce is fully informed about health and safety measures and standards. Easily understood safety and emergency instructions should be provided to employees and contractors in advance.

4. In the EU, the BAT includes the appliance of hazardous waste safety management to the handling, storage, and the feeding of hazardous waste materials. For example, using a risk-based approach according to the source and type of waste, for the labelling, checking, sampling and testing of waste to be handled. (EIPPCB, 2010)

Hazard analysis

5. Hazards and potential exposures should be determined and appropriate controls should be in place to maintain employee health and safety. Hazards requiring the use of personal protective equipment (PPE) should be identified. Assessments such as job hazard analysis (JHA), job safety analysis (JSA), safety analysis reports (SAR), process hazard analysis (PHA), and job, task, and hazard analysis (JTHA), are recommended.

Access and hazard control

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

(a) Engineering controls to preclude worker exposure by removing or isolating the hazard. For example, ventilation or use of remotely operated material handling equipment;

(b) Administrative controls to manage worker access to hazards and establish safe working procedures. For example, security measures to prevent unauthorized or unprotected access to hazardous wastes on-site;

(c) PPE, when engineering or administrative controls are not feasible or do not totally eliminate the hazard.
7. These controls are designed to reduce and maintain employee exposure below national occupational exposure limit values. If these are not available, internationally recognized exposure levels should be considered.

8. Examples include: the Threshold Limit Value (TLV) occupational exposure guidelines by the American Conference of Governmental Industrial Hygienists (ACGIH); the Pocket Guide to Chemical Hazards by the United States National Institute for Occupational Health and Safety (NIOSH); Permissible Exposure Limits (PELS) by the Occupational Safety and Health Administration of the United States (OSHA); Indicative Occupational Exposure Limit Values (IOELVs) by European Union member states, or other similar sources.

9. For hazardous substances and health hazards for which there are no permissible or applicable exposure limits, the operators could use the published literature and material safety data sheets (MSDS) as a guide to determine an appropriate level of protection.

   **Personal protective equipment**

10. Employees, contractors and visitors to an installation should be provided with PPE where engineering control methods are not feasible to reduce exposure to permissible exposure limits. PPE should be selected to protect against any present or potential hazard and appropriate to the task-specific conditions and duration.

11. All personnel involved in hazardous waste operations should be fully aware of: equipment selection and use, maintenance and storage, decontamination and disposal, training and proper fit, donning and doffing procedures, inspection, in-use monitoring, programme evaluation, and equipment limitations.

   **Training**

12. Employees should be effectively trained to a level determined by their job function and responsibility. This should be carried out prior to them being permitted to engaging in hazardous waste operations that could expose them to hazardous substances, safety, or health hazards. Training activities should be adequately monitored and documented in terms of curriculum, duration, and participants.

13. The training should cover safety, health and other hazards present on the facility; use of personal protective equipment; work practices to minimize risks from hazards; safe use of engineering controls and equipment on the site; medical surveillance, including recognition of symptoms and signs that could indicate over exposure to hazards. Those engaged in hazardous emergency response should also be appropriately trained.
Medical surveillance

14. A medical monitoring programme should be implemented to assess and monitor employee health both prior and during employment. An effective programme should consider the following components as a minimum:

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

Emergency response

15. Emergency plans and procedures should be established for the protection of the workforce and public before hazardous waste operations begin. An Emergency Response Plan, ensuring appropriate measures to handle possible on-site emergencies and coordinate off-site response, should be in place. As a minimum, this plan should address the following:

(a) Pre-emergency planning and coordination with outside emergency responders;
(b) Personnel roles, lines of authority, training and communication procedures;
(c) Emergency recognition and prevention procedures;
(d) Safe distances and places of refuge;
(e) Site security and control procedures;
(f) Evacuation routes and procedures;
(g) Site mapping highlighting hazardous areas, site terrain, site accessibility and off-site populations or environments at potential risk;
(h) Decontamination procedures;
(i) Emergency medical treatment and first aid procedures;
(j) Personal protective and emergency equipment at the facility;
(k) Emergency alerting and response procedures;
(l) Documenting and reporting to local authorities;
(m) Critique of response and follow-up procedures.

16. Emergency equipment, such as fire extinguishers, self-contained breathing apparatus, sorbents and spill kits, and shower/eye wash stations should be located in the immediate vicinity of hazardous waste storage and processing areas.

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

18. Arrangements should be made to familiarize local authorities and emergency responders with the layout of the facility; properties of hazardous waste
handled at the facility and associated hazards; places where facility personnel
would normally be working; facility entrances and possible evacuation routes.
Arrangements agreed to by local authorities, hospitals and emergency
response teams should be described in the Emergency Response Plan.
ANNEX 4

COMMUNICATIONS AND STAKEHOLDER INVOLVEMENT
ANNEX 4 – COMMUNICATIONS AND STAKEHOLDER INVOLVEMENT

1. Stakeholders are those who see themselves as potentially affected by the operations of a facility. These can be individuals and groups on a local, national, or international scale and include neighbours, community organizations, employees, trade unions, government agencies, the media, non-governmental organizations, contractors, suppliers and investors.

2. Public communication is the providing of information through media sources, including brochures, websites, newspapers, radio and television. Stakeholder involvement is concerned with community members and others with an interest in the facility, through public meetings, presentations, advisory committees, and personal approaches. Both should form part of the normal operations of a plant.

3. Facilities should have clear objectives for working with stakeholders. This includes a realistic timescale for engagement, committing necessary resources and a willingness to find mutually beneficial outcomes.

4. Operators and regulatory authorities should be prepared to address public concerns over possible impacts of co-processing and strive to establish efficient communication methods to explain the activities. Operators planning on using hazardous waste should provide all necessary information to allow stakeholders to understand the use of the wastes in the cement kiln while illustrating the measures that would be implemented to avoid adverse impacts.
ANNEX 5

GENERAL RECOMMENDATION ON WASTE ACCEPTANCE AND PRE-PROCESSING OF HAZARDOUS WASTE FOR CO-PROCESSING
ANNEX 5 – GENERAL RECOMMENDATION ON WASTE ACCEPTANCE AND PRE-PROCESSING OF HAZARDOUS WASTE FOR CO-PROCESSING

WASTE ACCEPTANCE

1. Prior knowledge of wastes is necessary to ensure that the waste falls within the requirements of the facility's permit and will not adversely affect the process. Generators of hazardous waste should in most circumstances know the composition, nature and problems associated with their waste, ensuring that all relevant information is passed to those involved in its subsequent management.

2. Hazardous and non-hazardous waste acceptance comprises two stages: pre-acceptance (or screening) and on-site acceptance. Pre-acceptance involves the provision of information and representative samples of the waste to allow operators to determine suitability before arrangements are in place for acceptance. The second stage concerns procedures when the waste arrives at the facility to confirm previously approved characteristics.

3. Failure to adequately screen waste samples prior to acceptance and a confirmation of its composition on arrival at the installation may lead to subsequent problems. Inappropriate storage, mixing of incompatible substances, and accumulation of wastes could occur.

Pre-acceptance

4. A pre-acceptance, or pre-shipment screening, protocol should ensure that only properly and safely handled hazardous waste streams are approved for shipment to the facility. Such protocol is necessary to:

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

5. The operator should obtain information on the nature of the process producing the waste, including its variability. Other required descriptions include: composition (chemicals present and individual concentrations); handling requirements and associated hazards; the quantity and the form of waste (solid, liquid, sludge etc); sample storage and preservation techniques. Ideally, information should be provided by the waste generators. Alternatively a system for the verification of the information provided by any intermediaries should be considered.

6. Systems for the provision and analysis of waste representative samples should be in place. The waste sample should be taken by a competent technician and the analysis carried out by a laboratory, preferably accredited
with robust QA/QC methods and record keeping and a chain-of-custody procedure should be considered. The operator should carry out a comprehensive characterisation (profiling) and testing with regard to the planned processing for each new waste. No waste should be accepted without sampling and testing being carried out. The exception is unused, outdated or off-specification uncontaminated products that have appropriate MSDS or product data sheets.

7. A Waste Analysis Plan (WAP) should be prepared and maintained to document procedures used to obtain a representative waste sample and to conduct a detailed chemical and physical analysis. A WAP should address measures used to identify potentially reactive and incompatible wastes. It should include testing of a representative sample to qualify the waste for use at the facility (pre-acceptance) and to verify its constituents (acceptance). Further testing of samples taken during or after waste pre-processing or blending should be used to verify the quality of the resultant stream.

8. Operators should ensure that the technical appraisal is carried out by qualified, experienced staff who understands the capabilities of the facility.

9. Records of pre-acceptance should be maintained at the facility for cross-referencing and verification at the waste acceptance stage. Information should be recorded and referenced, available at all times, regularly reviewed and kept up to date with any changes to the waste stream.

**On-site acceptance**

10. On-site verification and testing should confirm waste characteristics with the pre-acceptance information. Acceptance procedures should address:

(a) Pre-approved wastes arriving on-site, such as a pre-booking system to ensure that sufficient capacity is available
(b) Traffic control;
(c) Check for documents arriving with the load;
(d) Load inspection, sampling and testing;
(e) Rejection of wastes and the discrepancy reporting procedures;
(f) Record keeping;
(g) Periodic review of pre-acceptance information.

11. Wastes should not be accepted without detailed written information identifying the source, composition and hazard levels.

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

13. If sufficient storage capacity exists and the site is adequately manned, suitably qualified and trained personnel should supervise the receiving of hazardous wastes. All wastes received should be treated as unknown and hazardous until compliance with specifications has been positively verified.

14. A suitable description should accompany hazardous waste delivery including: name and address of the generator; name and address of the transporter; waste classification and description; volume and weight; and hazardous characteristics of the waste.

15. Documentation accompanying the shipment should be reviewed and approved, including the hazardous waste manifest, if applicable. Any discrepancies should be resolved before the waste is accepted. If they cannot be resolved, the waste should be rejected and sent back to the original generator, or at its request, to an alternate facility.

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

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

Inspection

18. Wastes should only be accepted at the facility after thorough inspection. Reliance solely on supplied written information should not be acceptable. Physical verification and analytical confirmation should be undertaken to ensure the waste meets permit specifications and regulatory requirements. All wastes, whether for processing or storage, should be sampled and undergo verification and testing, according to the frequency and protocol defined in the WAP, except for unused, outdated, off-specification or uncontaminated products.

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

(a) The identity and description of the waste;
(b) Consistency with pre-acceptance information;
(c) Compliance with the facility permit.

20. Techniques for inspection vary from simple visual assessment to full chemical analysis. The extent of the procedures adopted will depend upon waste chemical and physical composition and variation; known difficulties with certain waste types or of a certain origin; specific sensitivities of the
installation concerned (for example, certain substances known to cause operational difficulties); and the existence or absence of a quality controlled specification for the waste, among others. (Karstensen, 2008a)

21. The facility should have a designated sampling or reception area where containerised waste is unloaded if adequate space is available and temporarily stored for further sampling and sample analysis. Wastes should be segregated immediately to remove possible hazards due to incompatibility. Sampling should ideally take place within 24 hours of unloading. During this period, hazardous wastes should not be mixed, blended or otherwise mixed. Bulk wastes should be inspected and accepted for processing prior to unloading.

22. Sampling should comply with specific national legislation, where it exists, or with international standards. Sampling should be supervised by laboratory staff and in those countries where regulations do not exist, qualified staff should be appointed. Sampling should include well-established procedures such as those developed by the American Society for Testing and Materials (ASTM), the European Committee for Standardization (CEN), and the United States Environmental Protection Agency (EPA). A record of the sampling regime for each load and justification for the selected option should be maintained.

23. Samples should be analysed by a laboratory with a robust QA/QC programme, including but not limited to suitable record keeping and independent assessments. Analysis should be carried out at a timescale required by facility procedures. In the case of hazardous wastes this often requires the laboratory to be on-site.

24. Typically, waste should be sampled and analysed for a few key chemical and physical parameters (fingerprint analysis) to substantiate the waste composition designated on the accompanying manifest or other documents. The selection of key parameters must be based on sufficient waste profile knowledge and testing data to ensure accurate representation. When selecting fingerprint parameters, consideration should be given to those that: identify unpermitted wastes; determine suitability within the facility’s operational acceptance limits; identify potential reactivity or incompatibility; indicate any changes in composition that had occurred during transportation or storage. Should fingerprint testing results of a given waste stream fall outside the established tolerance limits, the waste may be re-evaluated for possible acceptance to prevent the unnecessary movement of waste back and forth between the generator and the installation. Re-evaluation should consider facility conditions for storage and processing; additional parameter analysis deemed appropriate by the operator and established in the WAP; permit requirements.

25. The inspection scheme may include: assessment of combustion parameters; blending tests on liquid wastes prior to storage; control of flashpoint; and screening of waste input for elemental composition, for example by ICP, XRF
and/or other appropriate techniques, in accordance to waste types and characteristics, and the facility waste acceptance criteria. (Karstensen, 2008a)

26. Wastes should be moved to the storage area only after acceptance. Should the inspection or analysis indicate a failure to meet the acceptance criteria, including damaged or unlabelled drums, such loads should be stored in a quarantine area, allocated for non-conforming waste storage, and dealt with appropriately.

27. All areas where hazardous waste is handled should have an impervious surface with a sealed drainage system. Attention should be given to ensuring that incompatible substances do not come into contact resulting from spills from sampling, for example, within a sump serving the sampling point. Absorbents should be available.

28. In accordance with national legislation and practice, suitable provisions should be made to verify that wastes received are not radioactive, such as the use of plastic scintillation detectors.

29. After acceptance, containerised hazardous waste should be labelled with the arrival date and primary hazard class. Where containers are bulked, the earliest arrival date of the bulked wastes should be indicated on the bulk container. Each container should be given a unique reference number for implant tracking.

**Non-conforming waste**

30. The operator should have clear and unambiguous criteria for the rejection of wastes, including wastes that fail to meet the acceptance criteria, and damaged, corroded or unlabelled drums. A written procedure for tracking and reporting such non-conformance should include notification to the customer or waste generator and competent authorities.

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

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

32. Wastes not fulfilling the acceptance criteria of the plant should be sent back to the waste generator, unless an agreement is reached with the generator to ship the rejected waste to an alternative authorised destination.
In-plant tracking system

33. An internal wastes tracking system and stock control procedure should be in place, starting at the pre-acceptance stage, to guarantee the traceability of waste processing and enabling the operator to:

(a) Prepare the most appropriate waste blend;
(b) Prevent unwanted or unexpected reactions;
(c) Ensure that the emissions are either prevented or reduced;
(d) Manage wastes throughput.

34. The tracking system, which may be a paper-based, electronic, or a combination of both, should trace the waste during its acceptance, storage, processing and removal off-site. At any time, the operator should be able to identify the location of a specific waste on the facility and the length of time it has been there. Records should be held in an area removed from hazardous activities to ensure their accessibility during any emergency.

35. Once a waste has entered bulk storage or a treatment process, tracking individual wastes will not be feasible. However, records should be maintained to ensure sufficient knowledge is available as to what wastes have entered a particular storage facility. For example, to avoid incompatibility with incoming wastes, it is necessary to keep track of residues building up within a vessel between de-sludging operations.

36. For bulk liquid wastes stock control should involve maintaining a record of the route through the process. Waste in drums should be individually labelled to record the location and duration of storage.

37. The in-plant waste tracking system should hold a complete record generated during pre-acceptance, acceptance, storage, processing and removal off-site. Records should be kept up to date to reflect deliveries, on-site treatment and dispatches. The tracking system should operate as a waste inventory, stock control system and include as a minimum:

(a) A unique reference number;
(b) Details of the waste generator and intermediate holders;
(c) Date of arrival on-site;
(d) Pre-acceptance and acceptance analysis results;
(e) Container type and size;
(f) Nature and quantity of wastes held on-site, including identification of associated hazards;
(g) Details on where the waste is physically located;
(h) Identification of staff who have taken any decisions on acceptance or rejection of wastes.
38. The system adopted should be structured to report on:
   (a) Total quantity of waste present on-site at any one time, in appropriate units;
   (b) Breakdown of waste quantities being stored pending on-site processing;
   (c) Breakdown of waste quantities on-site for storage only, that is, awaiting transfer;
   (d) Breakdown of waste quantities by hazard classification;
   (e) Indication of where the waste is located relative to a site plan;
   (f) Comparison of the quantity on-site against total permitted;
   (g) Comparison of time the waste has been on-site against permitted limit.

WASTE STORAGE AND HANDLING

39. After deciding the waste’s suitability, the operator should have systems and procedures in place for transfer to appropriate storage safely.

40. Considerations for waste storage on the installation should include:
   (a) Location of storage areas;
   (b) Storage area infrastructure;
   (c) Condition of tanks, drums, vessels and other containers;
   (d) Stock control;
   (e) Segregated storage;
   (f) Site security;
   (g) Fire risk.

Design considerations

41. Transfer and storage areas should be designed to handle accidental spills. This may require that:
   (a) To prevent spills from spreading or seeping into the soil, storage areas should have adequate boundaries and be adequately sealed, impermeable and resistant to the stored waste materials;
   (b) All spills should be collected, placed in a suitable container, and stored for disposal in the kiln;
   (c) If a spill occurs, incompatible wastes should be prevented from mixing;
   (d) All connections between tanks should be capable of being closed by valves. Overflow pipes should be directed to a contained drainage system such as a bounded area or another vessel;
   (e) Leak free equipment and fittings should be installed whenever possible;
   (f) Measures to detect leaks and appropriate corrective action should be provided;
   (g) Contaminated runoff should be prevented from entering storm drains and watercourses. Any runoff should be collected and stored for disposal in the kiln;
(h) Adequate alarms for abnormal conditions should be provided.

42. Storage design should be appropriate to maintain waste quality for the complete storage period. Segregated storage should be in place to prevent incidents from incompatible wastes and as a means of preventing escalation should an incident occur. Individual storage requirements on a particular installation will be dependent on a full assessment of risk.

43. Within the facility, specific storage area characteristics should reflect the properties of the waste that poses the greatest risk that can be accepted. In general, the storage criteria should also take into account the unknown nature and composition of wastes, as this gives rise to additional risks and uncertainties. In many cases, this uncertainty means that higher specification storage systems are applied for wastes than for well-characterised raw materials.

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

45. For containerised wastes, the design should be such to prevent accumulation of hazardous wastes beyond the allowable storage timescale. For liquid wastes, mixing or agitation to prevent settling of solids should be considered. It may be necessary to homogenise tank contents with mechanical or hydraulic agitators. Depending on the waste characteristics, some tanks may need to be heated and insulated.

46. The construction, material selection and design of equipment, such as tanks, pipelines, valves, and seals should be appropriate for the characteristics of the waste. They should be sufficiently corrosion proof, and offer the option of cleaning and sampling.

47. Adequate ventilation should be provided in consideration to applicable work exposure guidelines. Periodic monitoring should be considered for open stored wastes that may emit VOC.

48. A fire protection system approved by local authorities, for example, a local fire department, should be in place. Automatic fire detection systems should be used in waste storage areas as well as for fabric filters and electrostatic precipitators (ESP), electrical and control rooms, and other identified risk areas. Continuous, automatic temperature measurement of the surface of wastes in the storage pits can be used to trigger an acoustic alarm to indicate temperature variations.

49. Automatic fire suppression systems should be used when storing flammable liquid waste and in other risk areas. Foam and carbon dioxide control systems provide advantages in some circumstances, for example, for the storage of flammable liquids. Water systems with monitors, water cannons with the option to use water or foam, and dry powder systems are commonly used.
Operational considerations

50. Written procedures and instructions for the unloading, handling, and storage of wastes on-site should be in place. It should be ensured that chemically incompatible wastes are segregated. Compliance should be audited regularly.

51. To avoid the need for additional handling and transfer hazardous wastes should be stored in the same containers (drums) that were used for delivery.

52. Designated routes for vehicles carrying specific hazardous wastes should be clearly identified within the facility. On-site transportation should minimize risk to the health and safety of employees, the public and the environment. The operator should ensure that vehicles are fit for purpose with respect to compliance with relevant regulations.

53. All loads should be properly identified, segregated according to compatibility (so that any potential spills do not create chemical safety hazards), and secured to prevent sliding or shifting during transport. Personnel should be directed and trained to use equipment only as intended, and not to exceed the rated capacity of containers, vehicles, and other equipment.

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

55. Containers should be kept in good condition, free of dents, not leaking or bulging, and closed not in use. Container storage areas should have at least a weekly inspection.

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

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

57. Safety measures that should be considered include:

   (a) Placing of uncontrolled combustible materials in storage areas should be avoided;
   (b) Where there is a risk that has not been avoided or controlled, standard safety signs and information signs should be in place;
(c) Emergency showers and eye wash stations should be provided within the work area for immediate emergency use following exposure to hazardous wastes. 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;

(d) Adequate alarms should be provided to alert all personnel about emergency situations;

(e) On site communication equipment should be maintained so that in case of a fire, the control room and the local fire department can be contacted immediately;

(f) Electrical equipment should be earthed and have appropriate anti-static devices in place.

WASTE PRE-PROCESSING

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

59. Pre-processing includes drying, shredding, grinding or mixing depending on the type of waste. It is usually carried out in a purpose-made facility, which may be located outside or inside the cement plant.

60. Liquid waste fuels are normally prepared by blending different products with suitable calorific values and chemistry, such as spent solvents or used oil. Only simple pre-treatment is usually necessary, such as the 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.

Design considerations

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

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

63. Health and safety assessments should be undertaken on operations to ensure equipment safety 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 operating studies.

**Operational considerations**

64. Although mixing and homogenisation of wastes can improve feeding and combustion behaviour, it can involve risks and should be carried out according to a prescribed preparation.

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

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

66. Crane operators should be capable of identifying potentially problematic loads, for example, baled wastes and discrete items that cannot be mixed or may cause loading and feeding problems. These can then be removed, shredded or directly blended (as appropriate) with other wastes.

67. General tidiness and cleanliness should be applied to enhance working environment and to allow potential operational problems to be identified in advance. The main elements are:

   (a) Systems to identify, locate and store wastes received according to their risks;
   (b) The prevention of dust emissions from operating equipment;
   (c) Effective wastewater management;
   (d) Effective preventive maintenance.

**PRE-PROCESSING PLANT CLOSURE/DECOMMISSIONING**

68. Closure is the period directly after the facility stops 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.

69. Operators should be required to properly 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 this, a closure plan should be prepared identifying the steps necessary to partially or completely close the facility, including:

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

70. 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 both human health and the environment.

71. To minimise decommissioning problems and associated environmental impacts, it is recommended for existing installations, where potential problems are identified, to put in place a programme of design improvements (EIPPCB, 2006). These design improvements should ensure that underground tanks and piping are avoided. If replacement is not possible operators should provide secondary containment or develop a suitable monitoring programme. A procedure for the draining and cleaning out of vessels and piping prior to dismantlement, among others, should also be provided.

OTHER ENVIRONMENTAL ASPECTS

Volatile organic compounds, odours and dust

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

73. Abatement techniques should be in place as required and countermeasures for noise and odours considered. Dust is usually reduced by bag filters while VOC emission control technologies, if needed, may include carbon adsorption, thermal or biological treatments, among others.

74. In the EU, BAT is to apply the following techniques to prevent or control the emissions of dust, odours and VOC in the waste treatment sector as a whole: restrict the use of open topped tanks, vessels and pits; use an enclosed system with extraction to suitable abatement plant; apply a suitably sized extraction system; correctly operate and maintain the abatement equipment; have leak detection and repair procedures in place; and reduce air emissions by using a suitable combination of preventive and/or abatement techniques (EIPPCB, 2006).
Drums and ferrous metals

75. Empty drums and ferrous metals removed by magnetic separators should be disposed of in an environmentally sound manner. Scrap metal not contaminated by chemicals or scheduled wastes can be recycled for steelmaking. Empty waste drums contaminated by chemicals or scheduled wastes in good condition can be sent to authorised/licensed drum washers/recyclers.

Wastewater

76. Discharges of wastewater to surface water should not result in contaminant concentrations in excess of local ambient water quality criteria, or in their absence, other recognized ambient water quality criteria. 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.

77. Discharges into public or private wastewater treatment systems should meet the pre-treatment and monitoring requirements of that sewer treatment system. It 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.

78. In the EU, BAT is to apply the following techniques to wastewater management in the waste treatment sector as a whole: reduce the water use and the contamination of water; avoid the effluent by-passing the treatment plant systems; collect spillages, drum washings, etc.; segregate the water collecting systems; have a concrete base in all the treatment areas; maximise the reuse of treated wastewaters; conduct daily checks on the effluent management system; carry out the appropriate treatment technique for each type of wastewater; achieve adequate water emission values before discharge by applying a suitable combination of techniques (EIPPCB, 2006).

EMISSIONS MONITORING AND REPORTING

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

80. When wastewater is discharged, a monitoring programme, with adequate resources and management overview, for wastewater and water quality should be developed and implemented to meet set monitoring objectives.
81. 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 carried out or supervised by trained individuals. Those permitted or certified for this role should conduct the analysis. 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.
ANNEX 6

GENERAL RECOMMENDATION ON
CO-PROCESSING OF HAZARDOUS
WASTE
ANNEX 6 – GENERAL RECOMMENDATION ON CO-PROCESSING OF HAZARDOUS WASTE

OPERATIONAL REQUIREMENTS

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

   **Feed point selection**

2. Adequate feed points should be selected according to relevant characteristics of the waste, including physical, chemical, and toxicological (see Figure 6A). Different feed points can be used, most commonly waste is introduced via:

   (a) The main burner at the rotary kiln outlet end;
   (b) A feed chute at the transition chamber at the rotary kiln inlet end (for lump fuel);
   (c) Secondary burners to the riser duct;
   (d) Precalcerine burners to the precalciner;
   (e) A feed chute to the precalciners (for lump fuel);
   (f) A mid kiln valve in the case of long wet and dry kilns (for lump fuel).

3. Liquid wastes are typically injected into the hot end of the kiln. Solid wastes may be introduced into the calcining zone at some facilities. This is mid-kiln for long kilns, and onto the feed shelf in the high-temperature section for preheater/precalciner kilns.

4. Solid wastes used as alternative raw materials are typically fed into the kiln system via the normal raw meal supply, the same as traditional raw materials. 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. Wastes containing volatile organic and inorganic components should not be fed via the normal raw meal supply unless controlled test runs in the kiln, or adequate laboratory tests, have demonstrated that undesired stack emissions can be avoided.

5. Combustible toxic compounds found in some hazardous waste, such as halogenated organic substances, need to be completely destroyed through proper temperature and residence time. In preheater/precalciner kilns, hazardous waste should generally be fed through either the main or the secondary burners. Hazardous and other wastes fed through the main burner, where conditions will always be favourable, decompose under oxidising conditions at a flame temperature of >1800°C (see Figure 6B). 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°C (UNEP, 2007). The kiln should 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 (cf. Directive 2000/76/EC). In the case of hazardous wastes with a content of more than 1 per cent halogenated organic substances (expressed as chlorine), the temperature should be raised to 1100°C for at least two seconds.

Figure 6A - Typical waste feed points

Possible feed points

PRECALCINER KILN
- Exhaust gas
- Raw meal
- Precalcer firing
- Kiln inlet firing
- Clinker

PREHEATER KILN
- Exhaust gas
- Raw meal
- Secondary firing
- Kiln inlet firing
- Clinker

GRATE PREHEATER KILN
- Secondary firing
- Nodules
- Granulating table
- Grate preheater
- Clinker

LONG WET AND DRY KILN
- Mid kiln firing
- Chain zone
- Raw meal
- Exhaust gas

Clinker
Figure B - Temperatures and residence times during cement manufacture

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Temperature and time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature at main burner of the rotary kiln</td>
<td>&gt;1450°C (material) &gt;1800°C (flame temperature)</td>
</tr>
<tr>
<td>Residence time at main burner</td>
<td>&gt;12-15 seconds &gt; 1200°C &gt;5-6 seconds &gt; 1800°C</td>
</tr>
<tr>
<td>Temperature at precalciner</td>
<td>&gt; 850°C (material) &gt;1000°C (flame temperature)</td>
</tr>
<tr>
<td>Residence time at precalciner</td>
<td>&gt; 2-6 seconds &gt; 800°C</td>
</tr>
</tbody>
</table>

6. For hazardous waste feeding into the kiln, the following should be conducted (EIPPCB, 2010):

   (a) To use the appropriate feed points to the kiln in terms of temperature and residence time depending on kiln design and kiln operation;
   (b) 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;
   (c) 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;
   (d) To raise the temperature to 1100 °C, if hazardous waste with a content of more than 1 per cent of halogenated organic substances, expressed as chlorine, is fed into the kiln;
   (e) To feed wastes continuously and constantly;
   (f) To stop feeding waste when appropriate temperatures and residence times are not maintained or cannot be reached (at start-ups or shutdowns for instance), and whenever any emission limit value is exceeded.

**Kiln operation control**

7. To avoid operating problems within the kiln, the impact of hazardous waste on the total input of circulating volatile elements, such as chlorine, sulphur or alkalis, requires careful assessment prior to acceptance. Specific acceptance criteria for these components should be set by each facility based on the process type and on the specific kiln conditions.

8. The general principles of good operational control of the kiln system using conventional fuels and raw materials should also be applied to the use of waste. In particular, all relevant process parameters should be measured, recorded, and evaluated continuously. Kiln operators should undergo
appropriate training for the requirements related to the use of hazardous waste, including health, safety, and environmental emission aspects.

9. For operational disruptions 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.

10. The mineral content of the waste may affect the characteristics of the clinker. The raw mix composition should be adjusted accordingly to adhere 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 enrichment cycles of these compounds should only be considered if appropriate solutions for the management of the bypass dust generated have been identified.

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

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

ENVIRONMENTAL ASPECTS

Air emissions

12. Whether or not wastes are being used in a cement plant, dust (particulate matter), NOx and SO2 emissions cause the greatest concern and needs to be dealt with. Other emissions to be considered are VOC, PCDDs, PCDFs, HCl, CO, CO2, HF, ammonia (NH3), benzene, toluene, ethylbenzene, xylene, polycyclic aromatic hydrocarbons (PAH), heavy metals and their compounds (EIPPCB, 2010). Under some circumstances, emissions may also include chlorobenzenes and PCBs (SBC, 2007).

13. Control technologies should be implemented by the cement plant to ensure compliance to the emission limit as outlined in these guidelines.

Cement kiln and bypass dust

14. All cement plants generate a fine dust from the kiln line, collectively labelled cement kiln dust (CKD). CKD composition varies, 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.

15. 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).

16. To avoid disposal, most CKD and bypass dust is recycled directly back to the cement kiln or cement clinker grinder. In clinker manufacture, CKD partially offsets the need for raw materials such as limestone and natural rock constituents, thus avoiding the energy usage and emissions related to their extraction and processing. Periodically some dust may need to be 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.

17. Where appropriate CKD not returned to the production process may be recovered in various types of commercial applications, including agricultural soil enhancement, base stabilizing for pavements, wastewater treatment, waste remediation, low-strength backfill and municipal landfill cover (U.S. EPA, 2010). These applications depend primarily on the chemical and physical characteristics of the CKD.

18. The major factors determining 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.

19. Depending upon the level of contaminants of concern (for example, heavy metals, POPs), this waste can in some cases be hazardous waste for which special handling and disposal measures apply (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 PCDD/PCDF levels in the same magnitude as foods such as fish, butter, breast milk, and less than the maximum permissible concentration of 100 ng TEQ/kg for sewage sludge applied to agricultural land.

20. To ensure the protection of public health and the environment and to prevent groundwater contamination, bypass dust or CKD, discarded from facilities that use hazardous wastes as supplementary fuels or raw materials, should be analyzed for metal and organic leachate quality parameters if they are to be disposed of on land. 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 the air should also be controlled.
Emissions to water

21. In general, wastewater discharges are usually limited to surface run-off and cooling water only and cause no substantial contribution to water pollution (EIPPCB, 2010). Nevertheless, in the European Union the use of wet scrubbers is a BAT to reduce the emissions of SOx from the flue-gases of kiln firing and/or preheating/precalcining processes (EIPPCB, 2010). As such, the generation and management of wastewater shall subject to the requirements under Environmental Quality (Effluent) Regulations 2009, so as to limit the transfer of pollutants from the air into water.

End-product control

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

23. As a principle, co-processing should not alter the quality of the cement being produced. This means that the clinker, cement or concrete produced should not be used as a sink for heavy metals. There should be no negative impact on the environment as might be demonstrated with leaching tests on concrete or mortar, for example. The quality of cement should also allow end-of-life recovery.

24. 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, 2006).

25. As cement is blended with aggregates to form concrete or mortar, it is the behaviour of the metals within these building materials that is important for the evaluation of relevant environmental impacts of waste used in the production process. Studies have shown that metal emissions from concrete and mortar are low, and comprehensive tests have confirmed that metals are firmly incorporated in the cement brick matrix. In addition, dry-packed concrete offers high diffusion resistance, which further counteracts the release of metals. Tests on concrete and mortar have shown that the metal concentrations in the eluates are noticeably below those prescribed, for instance, by national legislation. Moreover, storage under different and partly extreme conditions has not led to any environmentally relevant releases, which also holds true when the sample material is crushed prior to the leaching tests. (EIPPCB, 2010).
26. In regard to the above, the main results of leaching studies done to assess the environmental impacts of heavy metals embedded in concrete are as follows (GTZ, 2006):

(a) The leached amounts of all trace elements from monolithic concrete (service life and recycling) are below or close to the detection limits of the most sensitive analytical methods;
(b) 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;
(c) The leaching behaviour of concrete made with different cement types is similar;
(d) 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;
(e) 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;
(f) 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);
(g) 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.

27. 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, 2006):

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

28. Careful selection and monitoring of the waste 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, 2006).

29. For "real-life" concrete and mortar exposure scenarios, different leaching tests and assessment procedures should be applied. Although standardized test procedures exist for waste management regulations and drinking water standards, there remains a need for harmonized and standardized compliance test procedures based on the exposure scenarios outlined above. It is recommended that a certified independent testing laboratory perform these at least annually.

MONITORING

30. Emission monitoring should be conducted 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):

(a) Standard methods of measurement;
(b) Certified instruments;
(c) Certification of personnel;
(d) Accredited laboratories.

31. 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).


Process monitoring

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

(a) Pressure;
(b) Temperature;
(c) O2;
(d) NOx;
(e) CO;
(f) SO2, when the SOx concentration is high (it is a developing technique to optimise CO with NOx and SO2).
34. 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):

(a) 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);
(b) Monitoring and stabilising critical process parameters, for example, homogenous raw material mix and fuel feed, regular dosage and excess O2.

Emissions monitoring

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

(a) Exhaust gas flow rate;
(b) Moisture (humidity);
(c) Temperature;
(d) Dust (particulate matter);
(e) O2;
(f) NOx;
(g) SO2;
(h) CO.

36. Continuous measurement of TOC is also 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.

37. Periodical monitoring at a minimum once per year is appropriate for the following substances:

(a) Metals (Hg, Cd, Tl, As, Sb, Pb, Cr, Co, Cu, Mn, Ni, V) and their compounds;
(b) HCl;
(c) HF;
(d) NH3;
(e) PCDDs/PCDFs.

38. The BAT according to EIPPCB (2010) is to carry out monitoring and measurements of process parameters and emissions on a regular basis, such as:

(a) Continuous measurements of dust, NOx, SOx and CO emissions;
(b) Periodic measurements of PCDDs/PCDFs and metals emissions;
(c) Continuous or periodic measurements of HCl, HF and TOC emissions.
39. It is also possible to measure and monitor NH3 and Hg continuously, and to
sample PCCDs/PCDFs and PCBs continuously for analysis from 1 to 30 days
(EIPPCB, 2010).

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

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

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

42. 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) and it is referred to the Updated
General Technical Guidelines for the Environmentally Sound Management of
Wastes Consisting of, Containing or Contaminated with Persistent Organic
Pollutants (POPs) (SBC, 2007).

Environmental monitoring

43. Justifiable concerns about the environmental impact from the plant may require
the implementation of an ambient air-monitoring programme. This should
assess levels of key pollutants identified as a priority for environmental 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 from significant interference from buildings
or other structures.

Reporting requirements

44. 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)

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

(a) 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;
(b) 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;

(c) 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).

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

(a) 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).

(b) 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.

(c) 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.

47. In order for monitoring reports to be used in decision making processes they should 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)
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