1. INTRODUCTION

At present, there are many cement factories in Germany which use, secondary materials (tyres, waste oil, waste plastic, liquid/solid, contaminated soils) in the production of cement. Key factors include favourable conditions inside rotary tube kilns, optimized process and safety technology and improved exhaust gas cleaning systems and a comprehensive control of the input substances. The requirements differ for each plant and these must be examined and defined as part of the licensing procedure in accordance with the Federal Immission Protection Act. This act states that environmental compatibility of an utilisation process should be assessed mainly on the basis of the expected emissions, the energy utilisation, and the effect on the environment. The measuring results show that the concentrations of trace elements, chlorbenzols, chlorphenols, PAH, PCDD and PCDF have not been proved or they have been far below the limit values in force in Germany.

2. INCINERATION OF HAZARDOUS WASTE IN CEMENT KILNS

Hazardous waste incineration is an engineered process that employs thermal oxidation at high temperature (normally 900 °C or higher) to destroy the organic fraction of waste. Minimum temperatures required for incineration range from 875 °C for incineration of municipal garbage to 1,400 °C for incineration of more stable organic compounds such as PCB, dioxin, and residues from polyvinyl halogenide production. Residence time at the high temperature must be at least 2 seconds. Producing cement clinker in cement kilns also involves high temperature burning. Liquid waste can be introduced into cement kilns using conventional oil burners; solid waste in the form of granulated material or powder can be fired like coal dust. In comparison with other types of hazardous waste incinerators, cement kilns possess several characteristics, which make them an efficient technology for destroying highly toxic and stable organic wastes.

Combustion gas temperatures and residence times in cement kilns exceed those of commercial hazardous waste incinerators. These high combustion temperatures and long residence times, along with the strong turbulence encountered in cement kilns, assure the complete destruction of even the most stable organic compounds. Burning of cement clinker requires a material temperature of 1,400 – 1,500 °C; consequently the flame temperature must be even higher in order to obtain heat transmission from flame to material. In the case of short kilns like preheated kilns and precalciner kilns the gas temperature in the burning zone is about 2,000 °C, at mid-kiln it is about 1,700 °C, and at the kiln exit it is about 1,100 °C. The gas retention time is about 5 seconds. The large size of kilns and the quantity of heated material present results in high thermal stability. In other words, temperatures within kilns change very slowly. Thus, even if a
cement kiln is forced into an emergency shut-down resulting from a loss of primary fuel or a severe malfunction, all hazardous waste in the kiln will be completely destroyed, provided automatic cut-offs prevent further injection of wastes. Cement kilns operate under alkaline conditions. Therefore, virtually all chlorine entering a kiln is neutralised of form sodium chloride, potassium chloride, and calcium chloride, all relatively non-toxic substances. Consequently, emissions of hydrogen chloride, a strongly acidic compound, are significantly lower than emissions from commercial hazardous waste incinerators.

3. EMISSION RANGES IN EXHAUST GAS FROM CEMENT KILNS

Emission data from kilns in operation is given in the next Table. The emission ranges within which kilns operate depend largely on the nature of the raw materials, the fuels, the age and design of the plant, and also on the requirements laid down by the permitting authority.

<table>
<thead>
<tr>
<th>Components</th>
<th>Emission value: from - to</th>
<th>Limit in permits in Germany</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust</td>
<td>1 – 15</td>
<td>15 - 20</td>
</tr>
<tr>
<td>HCl</td>
<td>0,3 – 5</td>
<td>10</td>
</tr>
<tr>
<td>HF</td>
<td>0,1 – 2,0</td>
<td>1</td>
</tr>
<tr>
<td>SO2</td>
<td>100 – 400</td>
<td>350 - 400</td>
</tr>
<tr>
<td>NOx</td>
<td>300 – 600</td>
<td>500 - 800</td>
</tr>
<tr>
<td>Hg</td>
<td>0,005 - 0,03</td>
<td>0,03 - 0,05</td>
</tr>
<tr>
<td>Cd + Tl</td>
<td>&lt; 0,001</td>
<td>0,05</td>
</tr>
<tr>
<td>Σ Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn.</td>
<td>&lt; 0,002</td>
<td>0,05</td>
</tr>
<tr>
<td>PCDD + PCDF (TE) [ng/m³]</td>
<td>0,001 - 0,01</td>
<td>0,05 - 0,1</td>
</tr>
</tbody>
</table>

Tabl 1: Emission in the exhaust gas from cement kilns

4. MONITORING

4.1 MONITORING - EMISSIONS

A distinction is made between continuous measurements and individual measurement. A further distinction is made between first-time and repeat measurements, function tests and calibrations, and measurement for special reasons, e.g. to determine the emissions of exhaust gas components which are not continuously monitored. The measurement-relevant parameters to be considered in measurement planning derive from regulatory requirements, e.g. the operating permit, information from the technical supervisory body responsible for the plant and from on-site inspection. All emission measurement results are reported in g/m³, mg/m³, ng/m³ as the mass of the emitted components related to exhaust gas volume at standard temperature and pressure conditions (273 K, 1013 hP), after deduction of the water vapour content. Typical kiln exhaust gas volumes expressed as m³/tonne of clinker (dry gas, 273 K, 1013 hPa). O₂-content is normally 10 %. 
To accurately quantify the emissions, continuous measurements are recommended for the following parameters:

- exhaust volume (can be calculated but is regarded by some to be complicated),
- humidity (can be calculated but is regarded by some to be complicated),
- temperature,
- Total dust,
- O₂ volume concentration
- NOx (Nitrogen oxides)
- SO₂ (Sulphur oxides)
- CO (Carbon monoxide)
- Hg (Mercury and its compounds)

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

- metals, semi-metals and their compounds,
- TOC (Organic substances)
- HCl (Hydrogen Chloride)
- HF (Hydrogen Fluoride)
- PCDD/Fs (Dioxins and Furans)

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

- BTX (benzene, toluene, xylene),
- PACs (polycyclic aromatic hydrocarbons), and
- other organic pollutants (for example chlorobenzenes, PCB (polychlorinated biphenyls) including coplanar congeners, chloronaphthalenes, etc.).

It is especially important to measure metals when wastes with enhanced metals contents are used as raw materials or fuels. It is appropriate to have measured all these substances on at least one occasion to provide data when applying for the plant’s first permit.

### 4.2 Monitoring Safe Combustion

The main requirements for low emissions are uniform kiln operation and constant operating conditions when using waste materials and waste oil. From this it follows that:

- the burning process has to be monitored continuously using modern process control technology,
- Waste materials require constantly fixed inspections on arrival and comprehensive preliminary homogenisation.
- Liquid media are sampled continuously through trickle tubes for quality control,
- the main parameters for analysis of the waste materials (calorific value, chemical composition, etc.) must be put into the process control system on a continuous basis,
• regulations of primary energy have to follow in reliance on secondary fuel data,
• the feed lance must be designed so that the waste fuel is injected centrally and is ignited at the flame front of the main fuel,
• The control units must allow the waste fuel to be supplied independently of the main fuel,
• waste fuels may only be supplied during normal continuous operation within the rated output range.

The description of a safety chain and safety regulations is necessary for supervising a firm combustion to recognize defects immediately and to avoid uncontrolled combustions of secondary fuels with suitable contact systems. The parameters of the “safety chain”, listed below, should be linked to one another by a computer-controlled logic system so that their effect on kiln operations and on emissions can be ascertained and the operation could be shut down at predetermined limits as a function of the degree of deviation from the set point value or the plant stoppage time, e.g.:

• Gas temperature less than 900 °C at kiln inlet,
• Temperature of material at kiln outlet less than 1250°C,
• CO- level above a value to be established by trial (Vol.%),
• Inadmissible control deviations in the setpoint/actual value comparison for the primary and secondary fuel feed,
• Raw-meal feed of less than 75 % of the max. possible quantity,
• Negative pressure before the exhaust gas fan below the value required at rated output,
• Permissible O₂ level lower than inspection measurements require,
• Permissible NOₓ level above 500 mg/m³,
• Failure of burner,
• Dust level above permissible limit.

### 4.3 MONITORING SECONDARY FUELS

Appropriate measures of emission restrictions start with a selection of waste fuels by the processing. The selection of rich, calorific valuable residual materials of production and the processing of household- and commercial - refuse to rich calorific valuable substitute fuels naturally depend upon with permit has given to each individual Cement plant. Therefore the following questions concerning the waste fuel could be asked:

• which residual are used ?
• out of which process do the waste materials come from ?
• which pollutants do the waste contain ?
• the data of the used substances (calorific value, water content, heavy metals, chlorine content, PCB, etc.).
• is the statements reliability durably guaranteed ?
• is a constant quality within a certain spectrum possible ?
• what is the expected emissions (PCB, Dioxin/Furan, heavy metals) ?
• how is the enrichment of harmful substances in clinker or cement?

A cement plant has to enclose the following documents when using waste fuels:

• a suitability proof of the processing plant, that it is recognized as a specialized waste disposal plant for the processing of residual materials of production
• proof, that the processing plant is suitable for this kind of processing and
• Documentation / Declaration of every single inorganic and organic substance of the wastes and the finished mixture of secondary waste fuels.

In the declaration analyses the background of the production process, the share of the whole mixture and possible specific features or divergences have to be described. The declaration analyses have to contain at least the following data from calorific value, heavy metal values, chlorine content, sulphure content, PCB content, etc... A plant diary, which must include the following information, has to be written every supplied charge of secondary fuels:

• the supplier’s name and adress,
• name and adress of the disposal’s producer,
• amount of the substances including its’ disposal key number,
• the supply’s date and time
• name of the employee which is responsible for the acceptance,
• date and number of the declaration analyses / corresponding confirmations.

The following trace elements which are contained in the input substances (used materials) are limited to median value and maximum value for every single waste in the following chart:

<table>
<thead>
<tr>
<th>Heavy metals in secondary fuels</th>
<th>Median Value [ppm] (kiln-mixed fuel)</th>
<th>Maximum Value [ppm] (single waste)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>Thallium</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Mercury</td>
<td>0,6</td>
<td>1,2</td>
</tr>
<tr>
<td>Antimony</td>
<td>25</td>
<td>60</td>
</tr>
<tr>
<td>Arsenic</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>Cobalt</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>Nickel</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>Selenium</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Tellurium</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Lead</td>
<td>70</td>
<td>200</td>
</tr>
<tr>
<td>Chromium</td>
<td>40</td>
<td>120</td>
</tr>
<tr>
<td>Copper</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>Vanadium</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Manganese</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Tin</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0,5</td>
<td>2</td>
</tr>
</tbody>
</table>
Table 2: Limits for heavy metals in waste fuel

Key factor is the quality of the substituted fossil fuel. A low difference in burden of pollutants between conventional fuel and waste fuel strengthens the advantage of coincineration. To compare scenario between “with and without waste fuel” it is advised to define an average fossil fuel content of heavy metals and use it for benchmarking. It can be used for direct comparison of different types of waste fuel qualities or even serve as basis for the development of a material specific standard. The standard could be defined as an average content of heavy metals and maximum content in the high calorific waste fuel.

5. CONCLUSION

Existing measuring results concerning the use of 50 - 75 % alternative combustibles and wastes (calorific value from 20-25 MJ/kg) have proved that the pollutants will be burnt safely if the liquids are screened and the solid waste-derived fuels (for example polychlorinated hydrocarbons) are spread in the gas flow. With regard to the emissions of chlorinated compounds such as PCB and dioxin, the exhaust values of the cement rotary kilns can only be achieved in other burning processes by the means of large-scale after-cleaning equipments. By utilizing waste materials the cement producing companies improve the cost-effectiveness of the production process, and the cement industry also makes a positive contribution to the environmentally compatible utilization of these materials. Strict input criteria of various secondary fuels are important for low emissions remain under limiting values.

6. REFERENCES


