Parallel session
Innovative energy efficiency examples of different industrial sectors –
Energy efficiency in the cement, metal and petrochemical industry

CO - PROCESSING OF WASTE AND
ENERGY EFFICIENCY BY CEMENT PLANTS

Richard Bolwerk
Council Government Münster
Domplatz 1-4, D 48128 Münster,
E-mail: richard.bolwerk@bezreg-muenster.nrw.de
ABSTRACT
The cement industry is net-shaped connected to the environment. The production process requires energy and that leads to emissions. Brown coal and hard coal are the predominant sources of energy in Germany. In the past, the specific need for combustibles approached the minimum of process engineering constantly. Another need for the protection of our natural resources, is the reduction of CO\(_2\). The reduction of the production costs could only be made possible with the use of particular energetic waste materials.
At present, there are many cement factories in Germany which use waste materials in the production of cement. Past experiences have shown that the cement industry can play an important role in the utilization of secondary fuels and the cement industry also makes a positive contribution to the environmentally compatible utilization of these materials.
The evaluation criteria for environmental compatibility are laid down in, among other places, the German Recycling and Waste Act. This act states that environmental compatibility of an utilization process should be assessed mainly on the basis of the expected emissions, the energy utilisation, the residues produced and the effect on the product. 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. The key environmental issues associated with cement production in the licensing procedure are air pollution and the use of energy. The clinker burning process is the main source of emissions and it is also the principal user of energy. There are some energy saving and energy recovery techniques for the main process in the cement industry, principally for the clinker burning process. These techniques also have to be considered in the determination of collateral regulations in the permission.
1 Introduction

The cement industry is net-shaped connected to the environment. The production process requires energy and this causes to emissions. Information on energy consumption including secondary fuels in the cement industry is relatively well known. Fossil fuels (e.g. coal, oil or natural gas) are the predominant fuels used in the cement industries. However, low-grade fuels such as petrol coke and waste derived fuels (traditionally waste oils, spent solvent, waste tyres) have been increasingly utilised in the recent years. More recently, the cement industry have also co-incinerated animal meals and animal fats.

The key environmental issues associated with cement production in the licensing procedure are air pollution and the efficient use of energy. The clinker burning process is the main source of emissions and it is also the principal user of energy. The requirements differ for each plant and these must be examined and defined as a 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 emission limits are laid down in accordance with the regulations described in TA Luft 2002 (German Clean Air Standards). If waste fuels are used in the clinker burning process as well as normal fuels, then regulation of the 17th BImSchV (Ordinance of the Federal Environmental Impact Act) also supply.

2 Incineration of waste Fuels

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 Energy Aspects by Burning CEMENT clinker

The production of Portland cement clinker is energy-intensive. Theoretically an average of 1.75 MJ of thermal energy is needed to burn 1kg Portland cement clinker. The actual requirement for thermal energy in modern plants is approximately 2.9 to 3.2 MJ/kg (BREFF 2001, CEMBUREAU 1997) depending form the process till 4 MJ/kg.

The production of cement involves four steps:
- Preparation of a material mixture;
- Thermal formation of clinker in the cement kiln;
- Clinker cooling;
- Grinding and mixing with additives to the cement quality required.

Most installations, use the dry process, which -for dry raw materials- is the most economical in terms of energy consumption. In Germany the cement clinker is burnt exclusively by dry process. As is shown by the plant layout in Fig. 1, the main components of a plant of this type are the preheater, calciner, rotary kiln and clinker cooler.

The conversion of the raw materials into clinker involves various processes at the following temperature ranges:

below 550°C: preheating, drying and dehydratation;
550 to 900°C: decarbonisation of CaCO$_3$ into CaO and CO$_2$;
Decarbonisation is an endothermic reaction. A flue gas temperature exceeding 1000°C is required.

900 to 1300°C: first recrystallisation or calcination reactions;
1300 to 1450°C: sintering and clinkerisation.
Sintering is an endothermic reaction. A flame temperature of 1800°C is required.

In a typical dry process, preheating and decarbonisation take place in a series of cyclones. The dry material enters at the top of the upper cyclone and moves downwards
through the cascade into the furnace. The hot flue gases from the kiln flow counter-currently. The cyclones provide a good heat and mass transfer, thereby enhancing the energy efficiency and flue gas cleaning.

Fuel energy is used in cement production mostly to burn the cement clinker. Electrical energy is used principally to drive the extensive grinding equipment and to operate the kiln systems.

There are some energy saving and energy recovery techniques for the main process in the cement industry, principally for the clinker burning process.

The heat recovery takes place by preheating the combustion air in the cooler while at the same time cooling the clinker, and by using exhaust the gas energy after the rotary kiln for calcining and preheating the raw meal in the calciner and preheater.

In the burning process in the rotary kiln sufficiently high material temperatures of ~ 1450 °C have to be reached for conversion of the clinker phases. In practice, fuels with an average net calorific value of at least h_u,m 20 – 22 MJ/kg are normally used in a main firing system. Preheating the air to 950 °C or more is therefore a very effective measure for recovering heat and reducing energy expenditure.

In the calciner the temperature of the kiln exhaust gas falls from about 1200 °C to the calcining temperature of about 850 °C (equilibrium temperature). To maintain the endothermic calcination reaction at this comparatively low temperature level, compared with the burning process, it is also possible to use here fuels of lower calorific value.

In a substitution of normal fuels by replacement fuels (waste materials), the first question which usually occurs relates to effect of the replacement fuels on the process conditions of the particular process. Particular attention has to be paid to the effects of using replacement fuels on process temperatures, exhaust gas masses, harmful substances and their levels, and specific energy expenditure, or efficiency for energy. Only then is it possible to discuss the possibilities of optimizing the process regime, e.g. recovery or by interconnected operation, for the conditions which have been altered by the substitution. The evaluation of a fuel is therefore depend not only on the nature of the fuel itself but to a considerable extent also on the mode of operation of the plant and on the heat recovery.
The fuel can be fed to the kiln at the following points:
1. Via the main burner;
2. At the transition chamber at the rotary kiln inlet via a feed chute (large pieces of fuel);
3. At the riser pipe via secondary fuel burners;
4. At the precalciner via precalciner burners;
5. At the precalciner via a feed chute (large pieces of fuel);

A preheater / calciner kiln system uses cyclones to preheat the raw materials, and an additional vessel, a calciner, which up to 60% of the total fuel to be burned in a secondary, lower temperature combustion zone. The addition of energy in the calciner increases the degree of calcination from 30 to 40% typical in a preheater kiln to 85 to 97%. Calcination begins at a temperature of about 815°C, and it is substantially completed at about 955°C.

Flue gases
The cement kiln is provided with 1, 2 or 3 stacks, depending on the process configuration. The main stack is always present.
The main releases from the production of cement are releases to air from the kiln system. These derive from the physical and chemical reactions involving the raw materials and the combustion of fuels. The main constituents of the exit gases from a cement kiln are nitrogen from the combustion air; CO2 from calcination of CaCO3 and combustion of fuel; water vapour from the combustion process and from the raw materials; and excess oxygen. In all kiln systems the solid material moves counter currently to the hot combustion gases. This counter current flow affects the release of pollutants, since it acts as a built-in circulating fluidised bed. Many components that result from the combustion of the fuel or from the transformation of the raw material into clinker remain in the gas phase only until they are absorbed by, or condensed on, the raw material flowing counter currently.

The adsorptive capacity of the material varies with its physical and chemical state. This in turn depends on its position within the kiln system. For instance material leaving the calcination stage of a kiln process has a high calcium oxide content and therefore has a high absorptive capacity for acid species, such as HCl, HF and SO2.

Part of the installations is equipped with a bypass and a bypass stack. A bypass is necessary when the chlorine content in the feed (raw material and fuel) is high. The presence of chlorine is a critical factor in the thermal process. Chlorine may react with calcium, giving CaCl2 that ends up in the clinker. However, most of it binds to sodium or potassium which leads to the formation of NaCl and KCl respectively. These latter salts sublime in the calcination zone and recrystallise in the decarbonisation zone, which results in an internal chloride cycle. As the chloride concentration rises, salt crusts may precipitate in the installation. This may lead to blockages, for example on the cyclone pipes, resulting in a kiln shutdown. The bypass is installed in the zone where the salt accumulation occurs. Part of the flue gas is removed here. Before emission the gas is dedusted by an electro precipitator or bag filter.

A third stack emits the air used for rapid cooling of the clinker. The gas is dedusted before emission into the atmosphere. This heated air may also be used as combustion air, which gives a more energy-efficient process.

In general the following energy information in the application is important

- total energy balance
- assessment of energy efficiency
- energy consumption
- energy saving plan
- description on energy use

4 Required Waste information in the application

The selection of rich calorific valuable residual materials 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.
The following questions concerning the waste fuel are important:

- which residuals are used and out of which process do the waste materials come from?
- which pollutants do the waste contain?
- the data of the used waste (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.

The following trace elements which are contained in the used materials for cement kiln are limited to median value and maximum value in the Table 2. The level for calorific value in waste fuel from manufacturing processes is $20 \pm 2 \text{ MJ/kg}$, the calorific value content for the high calorific part of municipal waste is fixed at $16 \text{ MJ/kg}$.

<table>
<thead>
<tr>
<th></th>
<th>Median Value [ppm]</th>
<th>Maximum Value [ppm]</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 (50-80)*</td>
<td>50 (100-160)*</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 (100-190)*</td>
<td>200 (300-400)*</td>
</tr>
<tr>
<td>Chromium</td>
<td>40 (60-125)*</td>
<td>120 (120-250)*</td>
</tr>
<tr>
<td>Copper</td>
<td>100 (120-350)*</td>
<td>300 (300-500)*</td>
</tr>
<tr>
<td>Vanadium</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Manganese</td>
<td>50 (100-250)*</td>
<td>100 (300-500)*</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>

* Exeption limits for Ni, Pb, Cr, Mn, Cu by high calorific part of municipal waste

*Table 2: Limits for heavy metals*
Key parameter 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 co-incineration. 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 Monitoring Combustion

The main requirements for 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 set point/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.

6 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 hPa), 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),
- temperature,
- Total dust,
- Hg (Mercury and its compounds)
- CO (Carbon monoxide), O₂ volume concentration
- NOx (Nitrogen oxides)
- SO₂ (Sulphur oxides)

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.).

1.1 Emission ranges

The use of various secondary fuels is always accompanied by extensive emissions measurement. The most important results from these measurements are summarized in Table 1. 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>14 - 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>

Table 1: Emission in the exhaust gas from cement kiln

7 Conclusion

Existing measuring results concerning the use of 50 - 75 % alternative combustibles and wastes (calorific value from 18 - 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.

For the assessment of waste utilisation which is harmless and in compliance with the regulations it is necessary to take into consideration the Ordinance on Incineration Plants Burning Waste and similar Substances (17. BImSchV) provided that residues materials are used based on the EU Directive 2000/76/EC on the incineration of waste of 4 December 2000, German Clean Air Standards -TA Luft 2002 and the Recycling and waste Act.

This means that in the authorization application all wastes, or groups of wastes which can be grouped together, must always be specified individually with the relevant point of
generation and analysis values as well as the calorific values. This requirement is particularly important when “synthetic fuels” are blended from various wastes outside the cement work. Evaluation based on the criteria of anticipated emissions, conservation of resources, energy balance and build-up of pollutants requires a comparative examination of the environmental effects of the individual waste.

8 References


