



**ecra**

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# NEWSLETTER

## Contents

New emission limits often require secondary abatement techniques	<b>p. 2</b>
Behaviour of organic compounds	<b>p. 3</b>

## Next ecra events to come

- Alkali-Silica Reaction  
October 24-25, 2006
- Chromate Reduction  
November 9, 2006
- Modern Clinker Cooler Technology  
December 6-7, 2006

# New emission limits often require secondary abatement techniques

The latest or ongoing developments in environmental legislation at EU level are leading to higher demands for emission abatement in the cement industry

The BAT reference document (BREF) which was published in 2001 describes demanding emission levels for cement plants. These emission levels should not be confused with emission limits which have to be stipulated by the authorities in permits. But the permitting authorities shall take these BAT emission levels into account when fixing emission limits for cement plants. It is left to the EU member states to specify, if necessary, how the technical nature of the installation and local conditions are to be taken into account additionally. The cement industry is of the opinion that the emission levels described are very demanding concerning dust and SO<sub>2</sub> and that they are not appropriate for NO<sub>x</sub>. The BREF document for the cement industry is already expected to be revised in 2007. Preparatory work at national and EU level is already under way.

BAT has been implemented in many EU member states in national legislation. In some member states it has led to lower emission limits, especially for dust, SO<sub>2</sub> and NO<sub>x</sub>.

## Reducing dust emissions

A BAT emission level of 20–30 mg/m<sup>3</sup> is specified for dust. This emission level can be achieved by using both electrostatic precipitators and fabric filters. Traditionally, electrostatic precipitators are used in the cement industry for reducing dust emissions in kiln exhaust gases. During the last years, when new filters have been built or filters have been renewed, fabric filters have also been playing an increasing role. In order to reduce investment costs, in some cases ESPs have been equipped with additional bag filters leading to the so-called "hybrid filter".

One advantage of the electrostatic precipitators is their low pressure drop. At normal clean gas dust levels they show a lower electrical energy consumption (including pressure drop of the fan) resulting in lower operating costs than fabric filters. Fabric filters are mainly used in cement works after cement mills, coal grinding plants and many small dust sources. At the end of the 1990's, in Europe the first application in kiln exhaust gas emerged. Some years later the scope was extended to the de-dusting of bypass gases. Due to lower emission limits, as well as

higher temperature-resistance in the available materials, there is a trend to install fabric filters if old filters have to be substituted.

## SO<sub>2</sub> abatement

The levels of SO<sub>2</sub> in the exhaust gases from cement kilns are essentially attributable to the content of readily volatile sulphur compounds as pyrites and marcasite in the raw materials used. The BREF document specifies 200 – 400 mg SO<sub>2</sub>/m<sup>3</sup> as the emission level for sulphur dioxide which can be achieved with Best Available Techniques. Up to an emission level of 1200 mg/m<sup>3</sup> of SO<sub>2</sub> lime hydrate addition is supposed to be BAT. Today there are a lot of experiences from cement plants using this technique. All in all the costs for this abatement measure are moderate, though high molar ratios of Ca(OH)<sub>2</sub>/SO<sub>2</sub> are necessary because the mechanism is based on a surface reaction.

For the reduction of very high SO<sub>2</sub> emissions the wet scrubber technique is BAT. As such high SO<sub>2</sub> emissions are exceptional, only a few cement plants are equipped with this technique. The reduction rate can be more than 90 % but costs are significantly higher than those for the lime hydrate addition.

## NO<sub>x</sub> abatement

Several primary measures like low-NO<sub>x</sub> burners, staged combustion or flame cooling are state-of-the-art for NO<sub>x</sub> abatement in the cement industry. However, depending on the initial emission level and the prevailing NO<sub>x</sub> limit the reduction potential is not sufficient. In some countries emission limits have been lowered

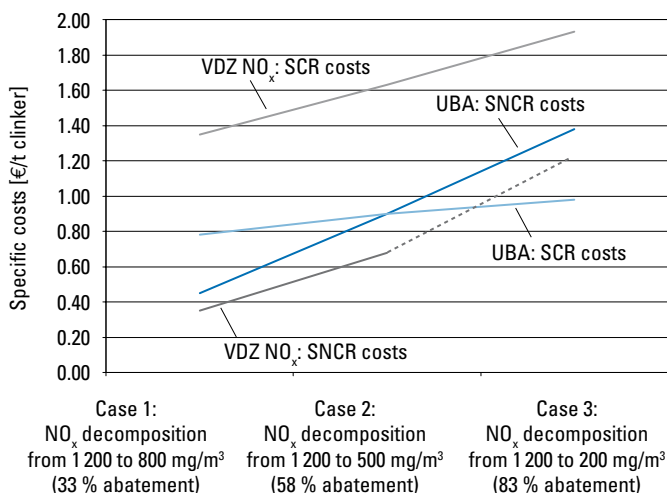


Fig. 1: SNCR/SCR cost comparison by the UBA (German Federal Environmental Agency) and the VDZ NO<sub>x</sub> abatement working group



Fig. 2: Visiting the limestone mine at Norcem's Brevik plant

significantly, especially if waste fuels are used. In these cases the SNCR technology is the first option. More than 80 cement kilns in Europe are already equipped with this technology. Operational experiences as well as recent research results show that it is very important to meet the temperature window of the reduction reaction (830 – 1050 °C). If the temperature is lower, unreacted ammonia can be emitted as ammonia slip. If the reducing agent is injected at a significantly higher temperature it can be burned to NO, leading to a higher molar ratio NH<sub>3</sub>/NO. Furthermore it is very important to mix the reducing agent as homogeneously as possible in the gas stream and the

riser duct. During the installation or optimization of a SNCR plant more attention should be paid to the reaction conditions in the injection area, the distribution of the reducing agent in the gas duct and the residence time of the reducing agent in the temperature window.

In the current BREF document the SCR (Selective Catalytic Reduction) process is not regarded as BAT. Only one SCR demonstration plant has been in operation since 2001. A detailed cost analysis by VDZ has shown that, regardless of the abatement rate, the SNCR process is always substantially less expensive than the SCR process (Fig. 1).

### Seminar in Norway

In June a seminar on Secondary Abatement Techniques was held in Porsgrunn/Norway. In the frame of the seminar the participants had the opportunity to visit the modern Norcem works in Brevik. One of the plant characteristics is that high amounts of secondary fuels are utilized and efficient abatement measures are installed to guarantee an environmental-friendly production. The most impressive experience during the plant tour was an excursion to the limestone mine which is more than 200 m below sea level (Fig. 2).

## Behaviour of organic compounds

### Overview about monitoring, formation and destruction in clinker burning process

Cement kilns co-incinerating waste are subject to conditions of the European Directive 2000/76/EC. Annex II.1 of this directive gives special provisions for cement kilns.

Concerning organic emissions an emission limit value of 10 mg/m<sup>3</sup> as daily average value is stated for TOC. TOC comprises all gaseous and vaporous organic substances in the exhaust gas. Exemptions may be authorised by the competent authority in cases where TOC does not result from the incineration of waste.

These exemptions are an inevitable prerequisite for operating a cement kiln as the TOC emissions are almost completely raw material related. Furthermore an emission limit value of 0.1 ng/m<sup>3</sup> is fixed for dioxins and furans. For carbon monoxide there is no generally admitted emission limit value but one can be set by the competent authority.

In ordinary firing systems the emissions of organic compounds and carbon monoxide can be taken as criteria for proper burning conditions. Such a direct correlation between

the exhaust gas level of organics and the quality of combustion is not applicable to cement kilns. Almost the complete organic compounds are introduced into the clinker burning process via the raw materials. The kiln feed passes counter-current to the combustion and kiln exhaust gases and intensive intermixing takes place. The temperature pattern and gas residence time in rotary kilns therefore offer particularly favourable conditions for complete destruction of organic compounds which are introduced via the fuels or are produced from them.

As a matter of fact the release of these organics from the kiln feed cannot be controlled via the operating conditions of the kiln system. During the preliminary heating process the organic constituents of the raw materials are liberated by the effect of temperature and emitted as



Fig. 1: ecura seminar on Behaviour of Organic Compounds in the Clinker Burning Process in Budapest



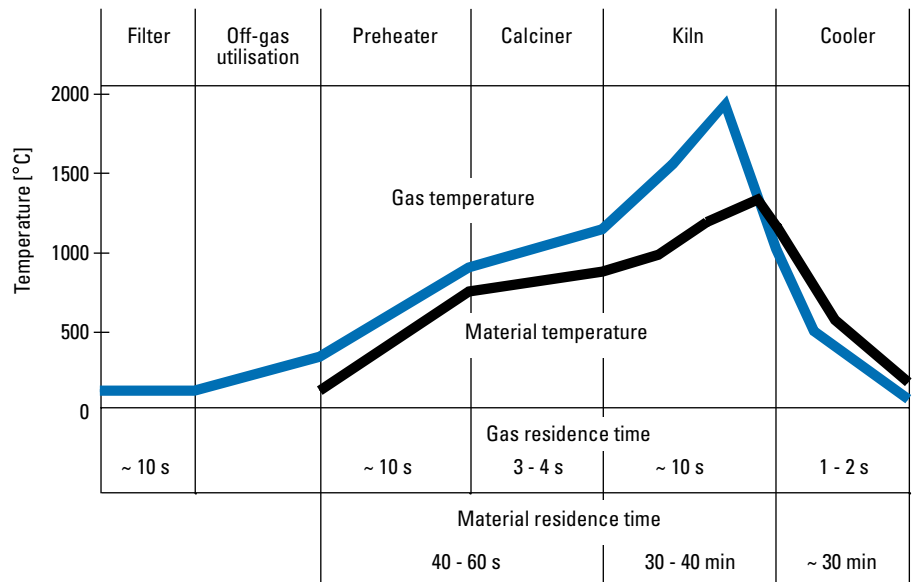
Fig. 2: Visit at the Duna-Dráva plant (HeidelbergCement) in Vác

organic compounds with the exhaust gas flow or are oxidized to carbon monoxide and carbon dioxide.

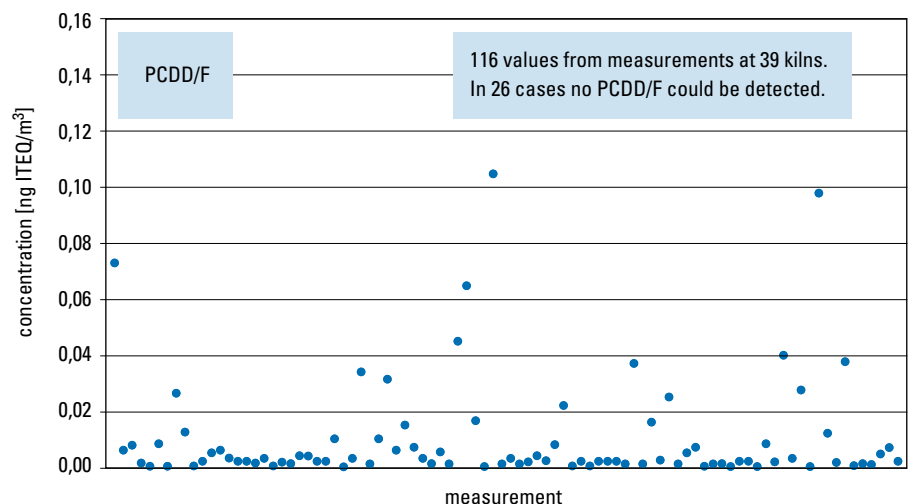
Depending on the characteristics of the organic compounds a part of them will be oxidised to carbon monoxide in a temperature range up to 700 °C. Only at temperatures above 700 °C a complete conversion to carbon dioxide is possible in the presence of oxygen. Therefore the CO levels in the kiln exhaust gas are substantially increased by the formation of carbon monoxide resulting from the raw material. Even under optimized combustion conditions the exhaust gas from rotary kiln systems in the cement industry can contain carbon monoxide and TOC which exceed the emission limit in the European Directive 2000/76/EC. On the other hand if an emission limit for CO has to be stated, the influence of the raw materials has to be taken into consideration.

Secondary raw materials may contain higher contents of volatile organic compounds. Depending on the substitution rate this can lead to higher organic emissions when added to the starting material (for example added in the raw mill). The increased release rates can be avoided if the secondary raw materials are added at higher temperatures, for example in the area of the calciner or kiln inlet. In this temperature range the organic compounds will be completely converted.

Further organic compounds of high concerns are: PCDD, PCDF, polychlorinated biphenyls (PCB), BTEX and PAH. Under the conditions prevailing in a cement kiln, i.e. flame temperatures of up to 2000 °C, material temperatures of up to 1450 °C and gas retention times of up to 10 seconds at temperatures between 1200 and 2000 °C all kinds of organic compounds fed to the main burner with the fuels are reliably destroyed. Gas temperatures from a precalciner burner are typically round 1100 °C, and the gas retention time is approximately 3 s. **Fig. 3** shows the typical gas and material temperature profile in cyclone preheater/precalciner systems. Because of these favourable conditions the PCDD/F emissions lie in almost every case below the emission limit value of 0,1 ng/m<sup>3</sup> (**Fig. 4**). This is the world wide strictest emission limit for dioxins and furans. It also applies to dedicated waste incinerators.



**Fig. 3: Typical gas and material temperature profile in cyclone preheater/precalciner systems**



**Fig. 4: Results of 116 dioxin measurements in the exhaust gas of cement kilns measured in 2004**

### Seminar in Hungary

In June 2006 a seminar on the behaviour of organic compounds was held in Budapest and Vác. On the first day of the seminar a comprehensive overview on the various sources of organic constituents was delivered. Apart from that the legal aspects as well as suitable abatement techniques were taken into consideration. A further highlight of the seminar was the visit of the cement plant of Duna-Dráva Cement Kft in Vác (**Fig. 1** and **2**).



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