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NEWSLETTER

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Carbon monoxide formation and burn-out during the clinker burning process

To prevent CO trips in electric precipitators different measures are taken into account

The formation and subsequent burn-out of carbon monoxide (CO) is inherent to any combustion process. Good combustion conditions provide good burn-out of the fuel and consequently of CO. This is also the case with the firing of cement kilns. However, unlike other combustion processes, organic constituents in the raw material for clinker production result in CO emissions, even under optimised combustion conditions. CO in the stack of cement kilns is therefore not an indicator for the quality of the fuel burn-out. The control of CO levels is nevertheless crucial in cement kilns in which electrostatic precipitators (ESPs) are used for dust abatement. For safety reasons ESPs have to be shut down for short periods in cases where fuel supply is unstable, e.g. due to blockages in the fuel preparation or feeding system. Plant operators have taken measures which provide good fuel feed, as well as optimised burner properties, configuration and kiln draft, in addition to appropriate CO monitoring in the process.

In firing systems, carbon monoxide and total organic carbon serve as an indicator for good combustion, especially of organic compounds. Low flue gas CO levels are therefore used as a criterion for the burn-out quality achieved by the firing system and hence are an indicator of low emission concentrations of organics. However, such a correlation between exhaust gas CO level and quality of combustion is not applicable to cement kilns.

Raw material-based emissions

Besides being fuels constituents, organic components are also introduced into the clinker burning process with the natural raw materials which, depending on the raw material deposit, may contain between 1,4 and 6 g of carbon per kg of clinker. Under the conditions prevailing in the preheater, these organic components – expressed as TOC (total organic carbon) – are liberated, part of them being emitted with the exhaust gas. They are present in the exhaust gas as carbon monoxide, carbon dioxide and, to a minor extent, in the form of volatile organic compounds (TOC). Carbon monoxide and TOC concentrations in the exhaust gas from cement rotary kiln systems range between 0,1 and 5 g/m³ (see **fig. 1**) and 5 and 100 mg/m³ respectively. Stack measurements and kiln balances have shown that the TOC and carbon monoxide emissions mainly originate from the raw meal-borne organic compounds rather than from the firing system. Given the chemistry and the thermal layout of the clinker burning process, it is therefore apparent that the clean gas CO and TOC levels are not suitable as a monitoring parameter for good combustion conditions. As the CO and TOC emissions originate predominantly from the organic compounds of the specific raw material deposit, there is no or only a very limited possibility of reducing the organics inputs.

Other impacts on CO emissions

Stable combustion in the firing of a cement kiln is provided by the oxidizing burning conditions, good fuel properties or the temperature profile in the riser duct and the calciner. As in any firing system, the fuel properties (ignition time, size, moisture) have an enormous influence on the burn-out of the fuels and therefore on possible CO emissions. This is of importance when designing for example SNCR installations, in which CO burn-out has to be seen in the context of NO_x reduction. Good hopper, transport conveyors and feeder design ensure that the feed rate of fuels is steady with minimal fluctuations. Otherwise, substochiometric combustion may occur which may lead to short term peaks of greater than 0.5 % CO.

Minimising CO-trips

ESPs have to be shut down during elevated CO levels in the flue-gases for safety reasons. In order to reduce ESP downtime, a systematic stepwise approach is needed. First of all, the main factors that can potentially influence CO trips have to be determined. This includes the determination of the CO level originating from the organics in the raw material, the control of the fuel feeding and the CO monitoring in the exhaust gas for internal process control. Such monitoring is adapted to the respective cement kiln with respect to reaction time, and is an integral part of the ESP's shutdown procedure. The ideal CO monitoring system has a short response time and should detect the CO concentration in the exhaust gases leaving the preheater, or at the kiln inlet in the case of long kilns.

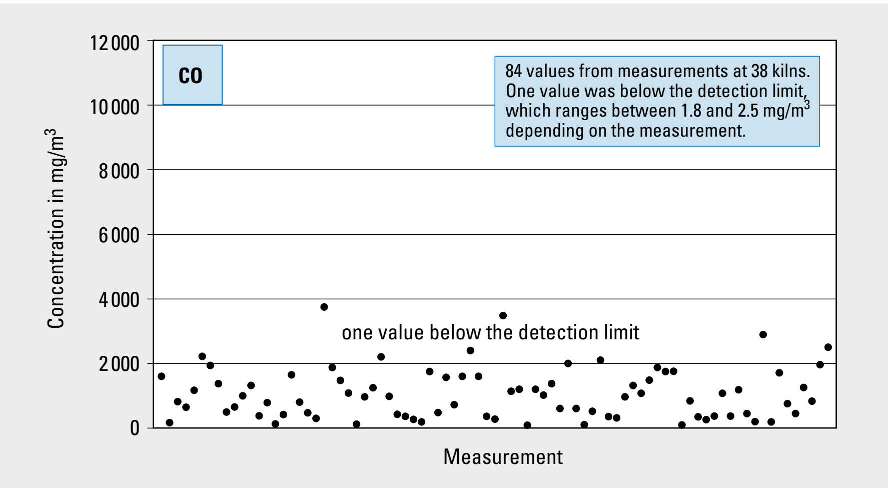

Fig. 1: CO emission concentration values measured in the clean gas

The monitoring system is characterised by its dead time, which has an impact on the proper timing for action to be taken; an analysis of the slope of the CO signal can provide additional information on when the ESP high tension system has to be shut down and when it can be put back into full operation again. Rapid in situ systems with response times of < 3 seconds are available, but these have limitations in high dust-laden gases. In general, a strict maintenance and calibration regime is essential.

If the CO trip cannot be avoided, any ignition sources, particularly the high tension equipment of the ESPs, require special attention. A shut-off of the high tension equipment as such is the last resort and is undesirable. Other potential ignition sources can be static loads caused by solid/solid friction or also fans, as is possible with any dust collector system.

In general, from a safety point of view, the critical gas concentration is > 8 % CO or – CH_4 – in the presence of more than 6 % O_2. However, in reality, the action level has to be significantly lower than the theoretical level, in order to take time delays in the whole monitoring and feedback system into account. The gas analysers have to be on-line during all operational phases; consequently plant downtime can be reduced for example by installing an appropriate backup system.

Tightened environmental liability scheme introduced

Regulations of the new Liability Directive require a well-designed environmental management

The new Directive 2004/35/CE on environmental liability with regard to the prevention and remedying of environmental damage sets a new framework for environmental liability in Europe. The date for its transposition into national law within the EU member states was April 21st 2007. The Directive is of high relevance for basically all industries because operators of industrial installations covered by the Directive have to take or finance preventive or remedial measures in case of damage to the environment. Moreover, local authorities and environmental protection organisations are provided with further rights. The Directive applies in particular to industrial operations covered by the IPPC Directive which also includes cement production. Pure grinding plants are also affected.

In the EU member states existing liability regimes cover damage to persons and property but not always to the environment as such. Now, for the first time in the EU, a new liability regime for damage to biodiversity, water and land has been set up by the so-called "Environmental Liability Directive". By this means an unprecedented level of prevention and precaution has been introduced.

Scope of the Directive

In principle the Directive applies to environmental damages caused by any occupational activity. Nevertheless a distinction between certain activities is made as shown in **fig. 1**. The cement industry is covered with all its activities, e.g. even pure grinding plants are included. Integrated

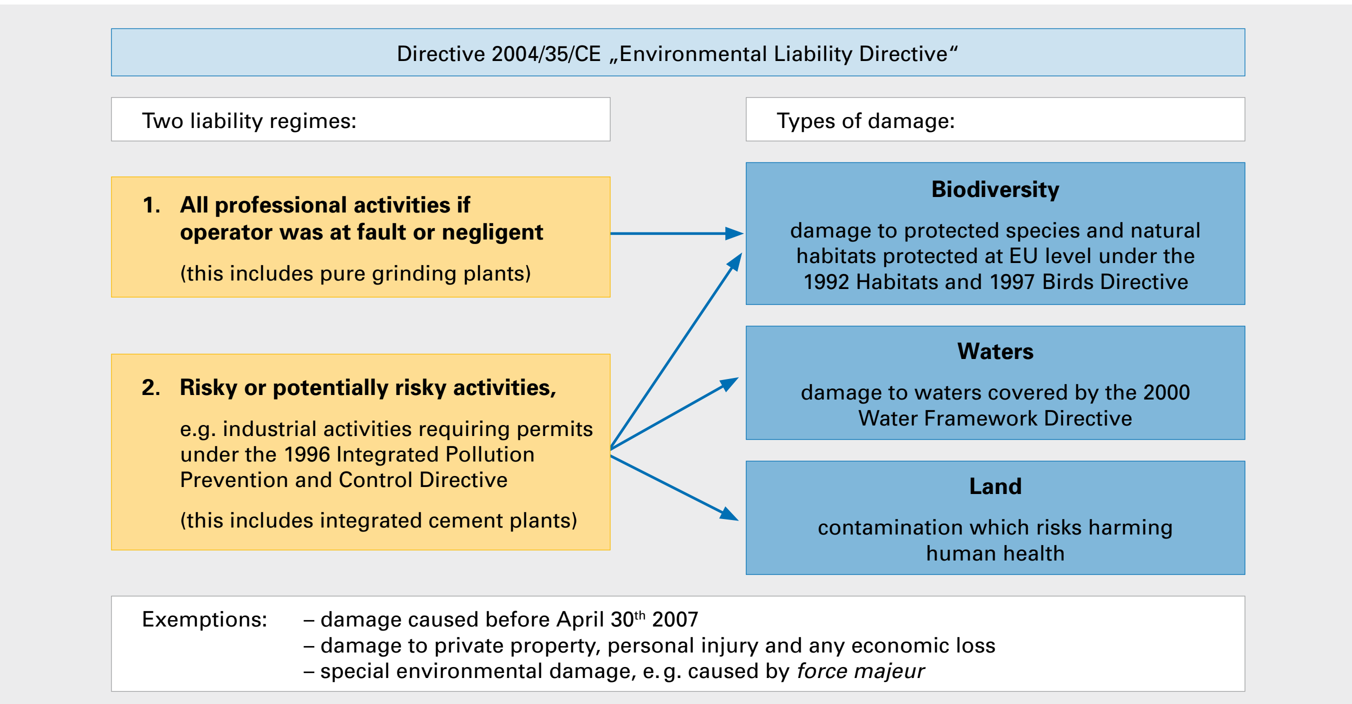

Fig. 1: Liability regimes and types of damage covered by the Directive

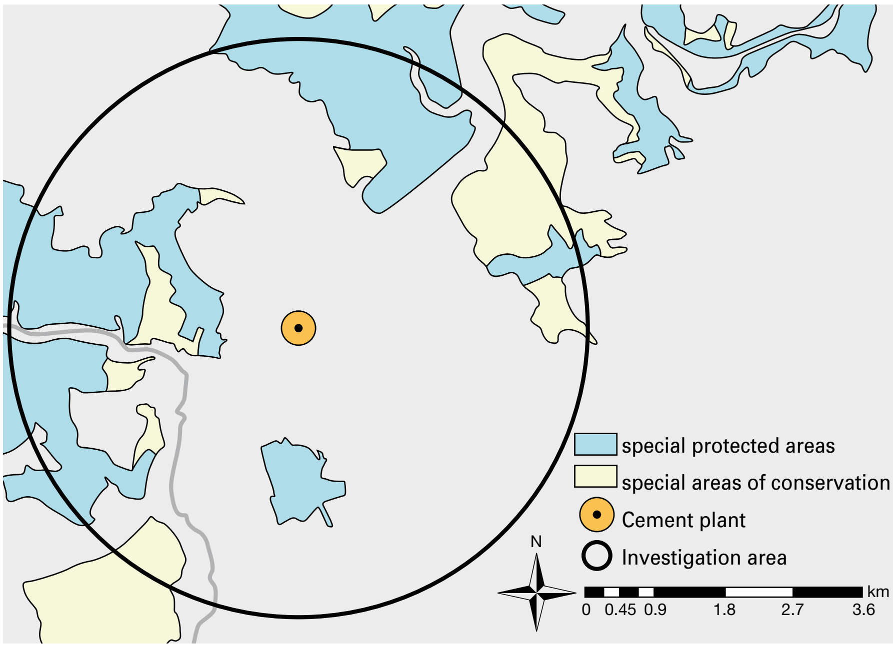

Fig. 2: Analysis of the surrounding area is useful

cement plants are explicitly addressed by Annex III of the Directive which defines all activities covered by the IPPC Directive as risky or potentially risky. As a consequence, according to the Directive any operator of such an activity can be held liable for environmental damages even if he has acted in compliance with permit and has not committed any fault. However, this will only apply to environmental damages where it is possible to establish a causal link between the damage and the activities of individual operators.

As shown in fig. 1, environmental damage includes damage to biodiversity (protected species and natural habitats), waters and land. While pure grinding plants can be held liable for biodiversity damages only, integrated plants are affected by damages to land and water as well. Exemptions are only foreseen for damage caused before April 30th 2007, or for damage that has been caused by *force majeure*, e.g. storms and floods. In general the Directive introduces a completely new liability scheme for the cement industry, which will have to adapt its environmental risk management schemes whenever necessary.

Key role for competent authority

Public authorities will play an important role under the proposed liability scheme. They are obliged to identify liable polluters and to ensure that they undertake themselves or finance the necessary preventive or remedial measures. Furthermore any natural and legal person and also public interest groups may call upon the authorities to act or challenge a decision at court.

In case of damage or an imminent threat of damage to the environment the operator is obliged to inform the competent authority immediately and to prevent further damage. Finally he has to take appropriate measures.

The main principle of these measures is the restoration of the environment to its baseline condition. Only if this is impossible does complementary remediation have to be undertaken.

Environmental risk assessment

Cement production and its emissions have always been of environmental relevance and have consequently been addressed by environmental legislation. Permits according to the IPPC Directive apply, and cement plants are operated complying with them. This applies to different kind of emissions. For example, dust emissions occur due to material handling in the plant or due to blasting in the quarry. The same applies to noise emissions. In order to avoid spills and leakages to water and soil, environmentally relevant liquids are handled with special care.

Due to the complexity of the operations and emissions linked with cement production, the thorough exploration of all internal and external environmental risks contexts is a challenging task.

Furthermore, under the new liability regime it is not easy for operators to insure themselves against environmental damage. Even though the Directive is in force there are hardly any appropriate financial insuring products. This is especially the case for damages that occur under full compliance with the permit. The Directive itself currently does not prescribe any compulsory insurance but the Commission will further decide on a system of harmonised mandatory financial security in 2010.

Given these aspects, it is helpful first to define and document the conditions and events that may represent threats and in the next step develop strategies to avoid them.

When adequate, the analysis of the area surrounding a plant is useful (see **fig. 2**). Protected areas under the Habitats Directive are made up of over 15.500 individual sites and cover almost 14 % of EU land territory. The nearer a plant is to such an area, the greater is the risk of potential damage. Special GIS tools, but also maps and web data, often available free, may help to evaluate the plant's own risk potential.

Further steps are the analysis of substances and operations on the plant itself which can pose a risk as well as the analysis of existing technical and organisational safety measures to control them. An environmental management system according to the ISO 14001 standard or an Eco-Management and Audit Scheme (EMAS) can be an option to control environmental performance in a continuous way.

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