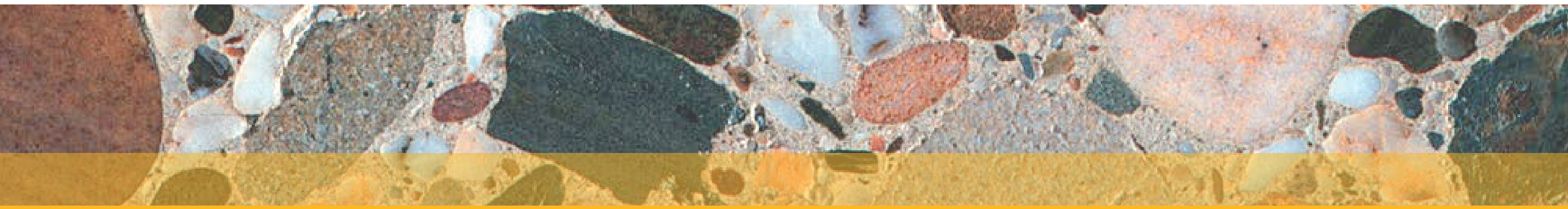
european cement research academy



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NEWSLETTER

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Efficient use of waste fuels in the cement manufacturing process

Pre-treatment and quality surveillance as decisive steps for efficient co-processing

Over the last decade the European cement industry has gained extensive experience in the use of alternative fuels in the clinker burning process. The simultaneous recovery process of energy and material is carried out in an environmentally responsible manner. This is proven on the one hand by the continuous and periodic control of the emissions of major pollutants. On the other hand, the alternative fuels are subject to very sophisticated quality assurance systems where necessary.

Producing clinker and cement is – like other industrial activities – a resource and energy intensive process. The use of alternative fuels reduces the corresponding amount of fossil fuels needed. The overall environmental impact of the operations is therefore also reduced. It is also important to note that the clinker burning process offers the unique possibility of a simultaneous recovery of energy and recycling of resources. This so-called co-processing of wastes is an advanced and innovative recovery process. In the latest revision of the Best Available Techniques Reference Document, co-processing in the cement industry is also considered as a best available technique (BAT) in Europe. Besides this, strict legal requirements have to be met by the operators of cement kilns in Europe.

Legal requirements

Cement kilns utilising waste in Europe as a fuel are subject to the European Directive on Industrial Emissions (2000/75/EU).

In addition to the general requirements on the environmentally responsible operation of industrial facilities, annex VI of the Industrial Emissions Directive (IED) covers the requirements on dedicated waste incinerators as well as the so-called co-incineration plants (i.e. industrial facilities such as cement kilns using waste fuels).

In so doing, the IED harmonises the European legislation for the incineration of waste. The co-incineration plants have to be operated according to the same environmental standards as the incinerators. The main idea of the IED and its annex VI is based on the regular control and monitoring of the emissions of the respective industrial facilities. **Table 1** compares the emission limits that have to be met by clinker kilns co-incinerating waste with the respective figures of the European Waste Incineration Directive (WID, 2000/76/EC), which has been replaced by the IED. Beside these legal requirements, the alternative fuels themselves also have to meet strict specifications.

	ELV [mg/Nm³]	
	IPPC / WID	New IED
Total dust	30	30
HCl	10	10
HF	1	1
NO_x	800 / 500 existing / new kilns	500 possible for long and lepol kilns until (max. 800)
Cd + Tl	0.05	0.05
Hg	0.05	0.05
Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V	0.5	0.5
Dioxins + Furans (ng/Nm³)	0.1	0.1
SO_2	50 raw material exemptions possible	50 raw material exemptions possible
Total organic carbon	10 raw material exemptions possible	10 raw material exemptions possible
CO	ELV can be set by the competent authority	ELV can be set by the competent authority

Table 1: Emission limits as per the former WID and the IED: Comparison

Turning waste into fuel

Selected waste materials with recoverable calorific value can be used as fuels in cement kilns if they meet strict specifications. In most cases a specific pre-processing of the waste has to be carried out in order to provide a suitable alternative fuel for the clinker burning process. Today, the cement industry in co-operation with waste management companies has developed suitable pre-treatment practises to produce alternative fuels. These sophisticated processes allow even mixed waste streams to be converted to high quality alternative fuels for cement plants. Quality control and testing procedures should be incorporated into the waste processing plant. They are essential for the implementation of a monitoring and surveillance procedure in the pre-treatment process. Important parameters that should be mentioned in this context include the calorific values of the alternative fuels, but the trace element content as well as the content of chlorine or sulphur can also play a decisive role.

Pre-processing of the waste materials

Pre-processing in general can be defined as operations which lead to the homogenisation of the chemical composition and/or physical characteristics of the materials. It is normally carried out with the aim of adapting the waste to suit selected pretreatment operation. In this context, typical mechanical processes such as sorting, shredding, grinding are applied.

It should also be pointed out that suppliers and manufacturers of pre-treatment facilities have been closely co-operating with the cement industry over the past years. This co-operation has contributed to the success story of sophisticated pretreatment processes today being able to guarantee a stable quality in the waste fuels. This development is also one of the reasons for the continuous increase of the use of alternative fuels in Europe. In 2011 the European cement industry was able to substitute more than 30 % of its overall thermal energy demand by suitable alternative materials (cf. **Fig. 1**).

Health and safety aspects

Co-processing in the cement industry must not have any negative impact on the health and safety of the work-

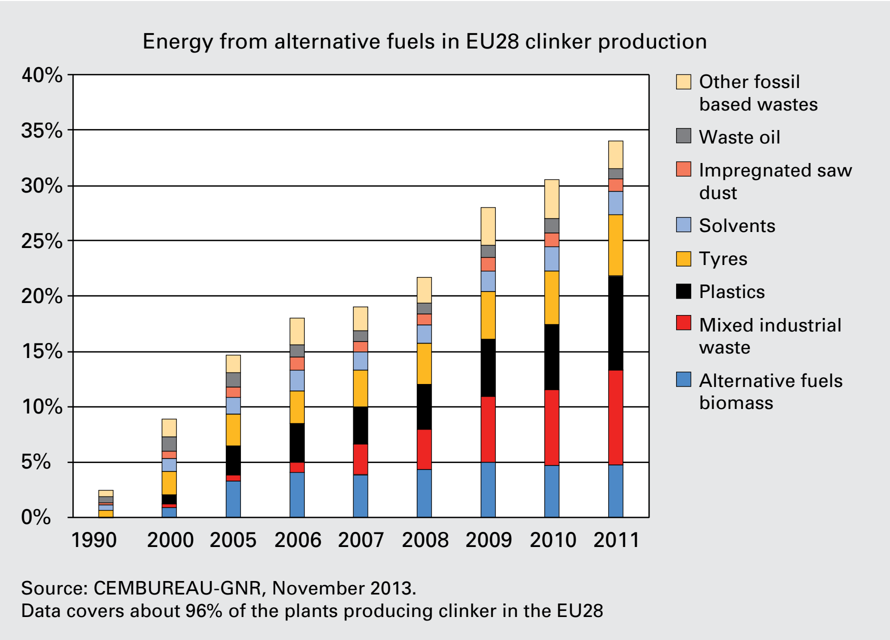

Figure 1: Use of alternative materials as thermal energy in the European cement industry

ers or the surrounding neighbourhood. It is therefore important that the respective pretreatment processes are also targeted at reducing occupational health and safety risks which might derive from the waste fuels. Furthermore, the feeding systems have to be adapted to the specific characteristics of the alternative fuels in order to avoid any potential risk. Due to the huge variety of the alternative fuels there is still a certain lack of standard parameters for assessing these potential risks (for example, self-ignition). In the worst case it might be necessary for the plant operator and plant designer to carry out measurements in advance in order to assess the potential risks.

Co-processing as a BAT procedure

As an almost waste free industrial process, clinker burning is highly suitable for applying the idea of co-processing. The demand for natural resources is thereby reduced, overall pollution is minimised and additional efforts for optional after-treatment of waste or the necessity for landfilling are avoided. Thus, co-processing is fully in line with the subject matter in the scope of the European Waste Framework Directive: It preserves natural resources, reduces emissions, uses the intake material in the product and recovers more than 80 % of the energy in the fuels.

These impressive figures show the potential contribution of the European cement industry to the modern and efficient recovery of alternative resources. Besides all other advantages, the industry can also play an important role with regard to environmentally efficient waste management.

Modern techniques used in the industry for quality control of cement

Methods such as X-ray diffraction and the Rietveld analysis provide new opportunities

Quality control of cement has a long tradition in Europe and worldwide. Already in the 19th century the first standards for cement were published. Since those early days many further developments have taken place. The Construction Products Directive and later the Construction Products Regulation set a framework to remove barriers to trade in the European market. National requirements have been consolidated in European standards and testing methods have been harmonised. In addition, techniques for quality control have also been improved. Traditional physical and chemical methods are still used, particularly as reference methods for quality control. Nevertheless, modern online and in-line analysis has become more and more established.

The cement industry realised very early that standardised rules are not only helpful for customers, but also for suppliers to ensure the quality of cement and thereby the safety and durability of construction works. Cement standards, published as early as in the late 19th century, were without doubt among the first standards ever for industrial products. Requirements on the product as well as corresponding testing methods were laid down at that time. Today we may smile at some of these old rules, for example, that 60 kg is convenient as the weight of one cement bag as this is "transportable with ease". Other original rules remain valid in Europe to this day. For example, mortar specimens for strength determination are still produced with "3 weight parts of normal sand and 1 weight part of cement", and testing is carried out "after 28 days' hardening". **Fig. 1** shows a historical "rupturing device" used in the 19th century for the determination of the tensile strength of mortar specimens.

European standards have become essential for the cement sector

The tradition of cement standardisation at an early stage was continued by CEN, the European Committee for Standardisation. In 2000, EN 197-1 "Composition, specifications and conformity criteria for common cements" was published as the first harmonised European standard for a construction product. EN 197-2 "Cement – conformity evaluation" was released in parallel.

Due to its importance for the safety of construction works, the assessment and verification of constancy of performance (AVCP) of cement follows the most rigorous AVCP sys-

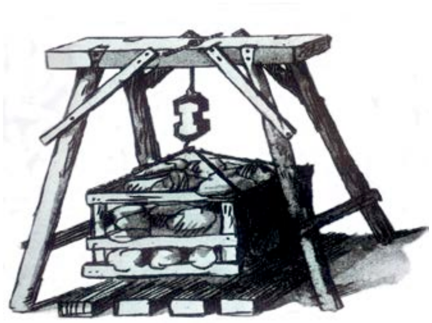

Figure 1: Testing the tensile strength of a cement mortar specimen in the 19th century

tem 1+. Cement and its production have to be controlled by a notified certification body. The duties of the manufacturer and of the certification body are described in EN 197-1 and EN 197-2. In particular, the manufacturer has to implement a factory production control (FPC) system and test samples of each cement according to the requirements given in EN 197-1. The certification body has to perform an initial inspection of the plant and of the FPC, initial testing of all cements, continuous surveillance, assessment and evaluation of the FPC, and audit testing of samples taken in the plant without prior notice.

The laboratory of the certification body usually applies reference methods for testing, most of them described in the European standard family EN 196, parts 1 to 10. These methods are classical physical techniques, for example, for the determination of setting time and strength development, and analytical methods of wet chemistry. However, as many reference methods require a lot of working time, they are often replaced by other techniques in cement plants. These should be automatable and fast in order to enable real-time production control. Their equivalence to the reference methods must of course be demonstrated in each case.

Modern methods for quality control of cement

Examples of modern automated analysis in cement plants are X-ray fluorescence analysis (XRF) and X-ray diffraction (XRD) combined with the Rietveld method. XRF is applied for the chemical analysis of, for example, cement and its constituents, in particular clinker. The chemical results can be used for the calculation of the "theoretical" phase composition of clinker and thus for the control of the clinker burning process. However, this method according to Bogue postulates completed chemical reactions in the kiln and does not for instance take into account the influence of burning conditions.

As an alternative, X-ray diffraction and the Rietveld analysis have become established in the cement industry over the past 15 years. The method was developed already in 1967 by Hugo M. Rietveld for crystal structure refinement using neutron scattering data. As a result of the improvement of X-ray detectors and computers needed for the calculation of the complex algorithms, the method can also be used today for quantitative phase analysis, for example, of clinker and cement. **Fig. 2** shows an example of a Rietveld analysis of a cement sample. The method provides information not only on the phase composition, but also on crystallographic details. For example, it is possible to distinguish between cubic and orthorhombic calcium aluminate C_3A as clinker phases. These modifications show a different hydraulic reactivity and can influence the hydraulic properties of cement, i.e. setting time, workability and microstructure development.

XRF and XRD can both be implemented as classical online methods in cement plants: Samples are automatically taken in the process and sent to a central laboratory, for example, using a pneumatic tube, for further preparation and analysis. The whole procedure is much faster and needs less manpower than traditional wet chemistry or clinker microscopy. A direct process control is possible although there is still a minor loss of time between the sampling and the availability of the results.

Inline testing starting to replace classical online analysis

As a new trend, inline methods which are directly implemented in the production process are increasingly being introduced in the cement industry. For example, the prompt-gamma neutron activation analysis (PGNAA) can be used to determine the chemical composition of raw material. For this purpose an analyser can be mounted directly on the belt conveyor, where the material is analysed continuously during transport in order to optimise stockpiling. Other examples of inline analysis are mill control systems directly placed at or on the mill. Inline methods are often less precise than online methods, but they have the advantage that no sampling and sample processing is necessary and that a lot of data can be used for continuous process control. However, the equipment should be robust to ensure high availability even under the rough conditions of the cement production process.

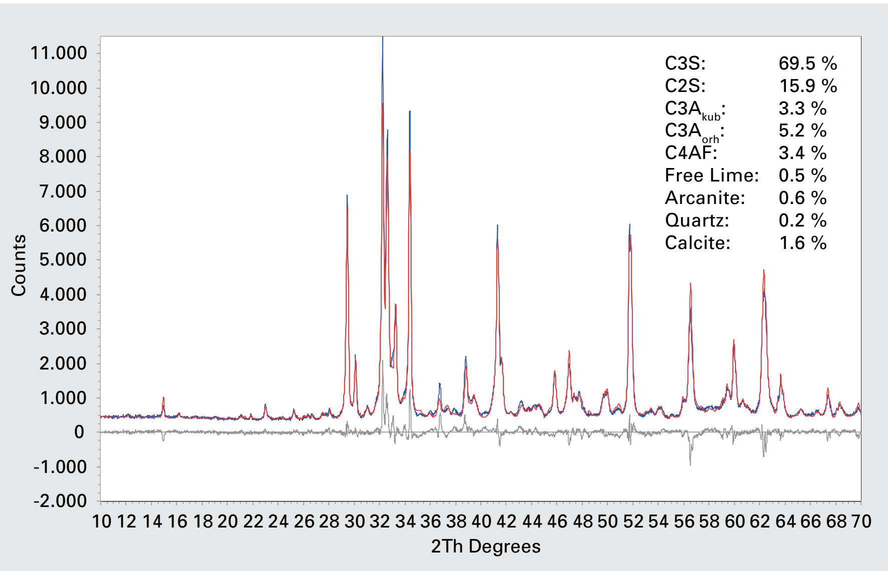

Figure 2: Rietveld analysis of a cement sample

ecra
european cement research academy

European Cement Research Academy

Tannenstr. 2 · 40476 Duesseldorf
P.O. Box 30 03 32 · 40403 Duesseldorf
Germany

Phone: +49 (0)211 2 39 83 8-0
Fax: +49 (0)211 2 39 83 8-500

info@ecra-online.org
www.ecra-online.org