EFFECTS OF THE USE OF SECONDARY MATERIALS ON EMISSIONS IN CLINKER PRODUCTION

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Introduction

The clinker burning process is very well suited for utilising secondary materials. The utilisation of those alternative materials permits complete material and energy recovery without any relevance for the environment or product-specific residuals being produced.

Behaviour of exhaust gas constituents

Table 1 summarizes individual exhaust gas constituents in relation to the crucial factors influencing the content of the respective constituents in the exhaust gas. The dust concentration is influenced by the precipitation behaviour of the air pollution control device. The content of heavy metal compounds in the exhaust gas is additionally determined by the input situation in the kiln.

Exhaust gas constituents	Influencing factor
Dust	Electrostatic precipitator, bag house filter
Heavy metals	Electrostatic precipitator, input
NO_x	Process
Total carbon, CO, SO_2, NH_3	Raw material
Dioxins and furans	Process

Table 1: Factors influencing the emission behaviour of different exhaust gas constituents

The generation of nitrogen oxides is inherent to the process. It is normally not influenced by the use of alternative materials. The decisive factor for the content of carbon monoxide and total carbon is the raw material composition. Moreover, depending on the respective locations, the raw material situation can effect the emissions of sulfur dioxide, ammonia and other organic compounds like benzene as well.

Toxic organic constituents such as dioxins and furanes are unaffected by the type of alternative fuels used. Their content in the clean gas of rotary kiln plants is extremely low.

Figure 1 shows a comparison of nearly 160 single measurements. The emission concentrations are plotted on the ordinate, the abscissa indicates the measurement number. The grey circles symbolise the measurement with regular fuels. The red squares describe the situation in case of using secondary fuels, and the yellow triangles indicate the results of the measurements with secondary raw materials.

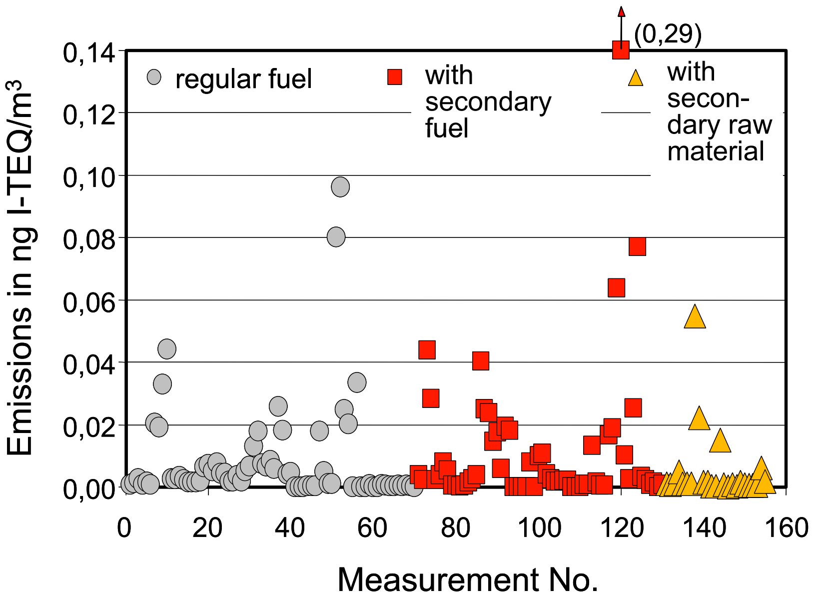

Figure 1: Dioxin and furan concentration measured by the Research Institute of the Cement Industry

All the organic compounds are destroyed completely during the clinker burning process. The use of alternative fuels as well as the recovery or substitution of raw materials has absolutely no effect on the measured emissions. All these findings are confirmed by the current measurements as well as those published in the environmental data of the German cement industry.

Emissions of heavy metals

The emission concentrations of the individual elements are determined by the input scenario, the behaviour in the plant and finally the precipitation efficiency of the air cleaning devices. The emissions of trace elements can be described on the one hand with emissions factors, Figure 2.

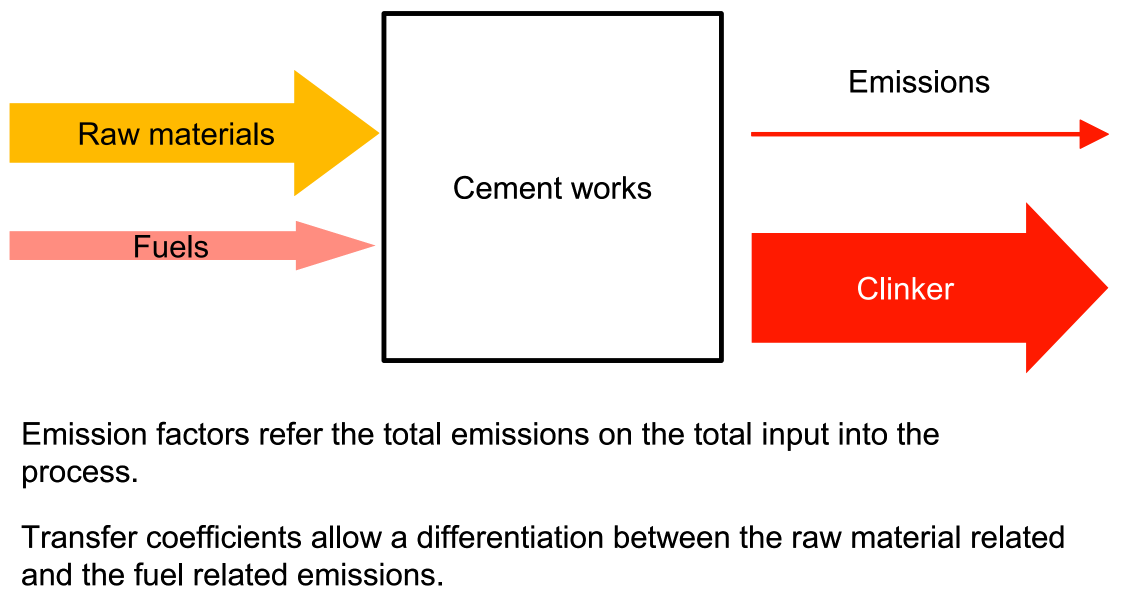

Figure 2: Emissions of the clinker burning process are due to the total input of raw materials and fuels

Emission factors can be determined directly from measured values by mass balancing the complete system. They describe the emitted mass proportion of a trace element brought into the process via raw materials and fuels. This summary way of looking at the emissions does however not allow the fuel related emissions to be distinguished from emissions caused by the raw material. Due to the fact that the cement industry is increasingly replacing standard fuels with secondary fuels such a differentiation is an issue of growing importance.

This question has led to the development of the transfer coefficients. These coefficients serve to calculate the proportion of trace elements from fuels emitted with the clean gas. In contrast to the emission factors, transfer coefficients can not be measured directly. They have to be determined based on calculations taking into account the material balances for partial systems of the burning process.

Figure 3 describes the procedure schematically. In a first step, the preheater and the rotary kiln are looked at separated from the dust collection. The reactions of the trace elements in each partial system are determined based on clinker binding and filter precipitation efficiencies. In a second step these individual results are combined arithmetically to get the final results.

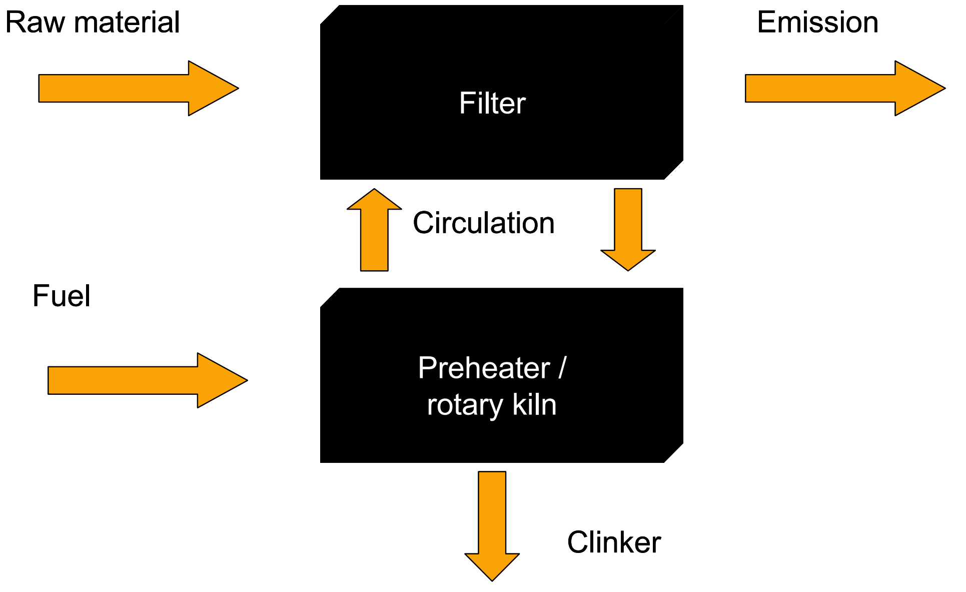

Figure 3: Mathematical modelling of material fluxes

Table 2 depicts emission factors and transfer coefficients for rotary kiln plants with cyclone preheaters. The bandwidths given for the emission factors are based upon a huge number of mass balance investigations conducted by the FIZ. The transfer coefficients have been calculated based on the representative data.

Component	EF (%)	TC (%)
Cd	< 0.01 - < 0.2	0.002
Pb	< 0.01 - < 0.2	0.002
Tl	< 0.01 - < 1.0	0.02
Sb	< 0.01 - 0.05	0.0005
As	< 0.01 - 0.02	0.0005
Mn	< 0.001 - < 0.01	0.0005
Co	< 0.01 - < 0.05	0.0005
Cu	< 0.01 - < 0.05	0.0005
Cr	< 0.01 - < 0.05	0.0005
Ni	0.01 - < 0.05	0.0005
V	0.01 - < 0.05	0.0005
Sn	0.01 - < 0.05	0.0005
Zn	0.01 - < 0.05	0.0005

Table 2: Emission factors (EF) und Transfer coefficient (TC)

A comparison between the given numbers indicates that the emission factors are orders of magnitudes higher than the transfer coefficients. This means that only a negligible amount of trace elements from fuels gets into the emission amount. Furthermore the values of the emission factors illuminate the high retaining efficiency of the whole process for trace elements. This enormous retention capacity also explains the fact that trace elements are only found in very small amounts during emission measurements. The current emission data of the German cement industry show that in about 80 % of all cases the measured values were below the detection limit.

One exception has to be mentioned - and that is mercury. The measured emission concentrations for mercury are primarily dependent on the respective operating conditions. Nevertheless the question whether the use of secondary materials has an impact on the mercury emissions is of great importance.

Figure 4 shows the comparison of a huge number of individual measurements that have been conducted at nearly 60 different kilns. The mercury emissions concentrations are plotted on the ordinate, the x-axis indicates the test series number. The red circles stand for the measurements with regular fuel. The yellow squares describe the situation in case of using secondary fuels and the few triangles in light-blue indicate the results with secondary raw materials. Based upon these experimental findings one can say that even for the highly volatile trace element mercury the emission level is not affected by the use of secondary materials.

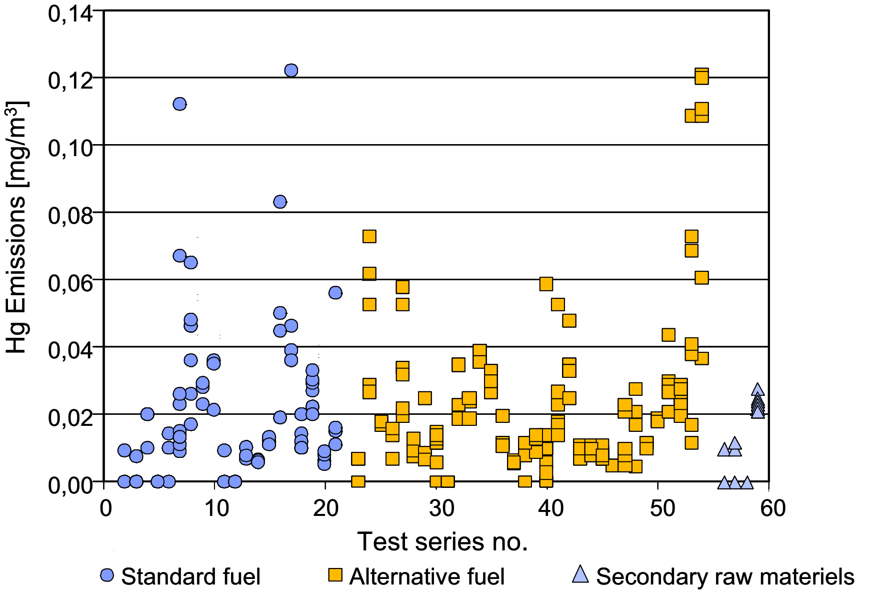

Figure 4: Mercury emissions with and without use of secondary material

Conclusion

Cement works utilize selected wastes, which have to suit the process. In addition to that, the emissions have to meet very stringent legal requirements when secondary fuels are used. Together with the particular features of the clinker burning process this finally leads to the recognition that the use of secondary materials leaves the emission level unchanged. Based upon these assumptions the use of alternative materials in the cement manufacturing process is ecologically beneficial without any doubt.