



Research article

Disposal of waste-based fuels and raw materials in cement plants in Germany and Switzerland – What can be learned for global co-incineration practice and policy?

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ABSTRACT

The limit value for emissions of total organic carbon (TOC) for incinerators in the European Union (EU) is 10 mg/m³. However, clinker burning is a material conversion process during which TOC emissions from the fuels occur concurrently with the thermal decomposition of organic material from the raw material mixture (limestone, marl, shale, etc.) in the preheater, which alone can emit more than 10 mg/m³. Therefore, the German legislature has created an exemption that allows authorities to set higher limit values for cement kilns if the cause of the higher emissions is the natural raw material mixture and not the co-incinerated waste. Separating the effects requires a test to determine the baseline emission of the natural raw material or waste raw material. Up until now, these tests were only used internally by companies. By applying such tests, the emissions from the fuels, particularly from waste-based fuels, can be determined, restricted and controlled. TOC emissions from natural materials cannot be avoided. In Switzerland and Germany these emissions are on average around 20–35 mg/m³. Switzerland has recently set a high TOC limit value of 80 mg/m³ for cement kilns, independent of the source of organic emissions, and even allows the use of polychlorinated biphenyl (PCB) contaminated soils as raw material (up to 10 mg/kg). This limit is too high and can result in unnecessary emissions of carcinogenic benzene, PCBs and other pollutants.

Both the natural raw materials and waste raw materials emit organic carbon. However, there is one major difference. The natural raw materials emit mostly aliphatic compounds at temperatures up to about 600 °C, whereas the organic compounds originating from waste-based raw material components can include hazardous pollutants like polychlorinated biphenyls (PCBs) and other persistent organic pollutants (POPs), which desorb in the preheater and are released into the environment. Therefore, waste raw materials such as soils contaminated with POPs or other semivolatile toxic chemicals cannot be introduced via the raw mill – (leading to desorption in the preheater) but need to be fed in the kiln inlet. Cement kilns treating POPs or raw materials with problematic semivolatile organics need strict control and possibly continuous monitoring for dioxins and other POPs.

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1. Introduction

The use of wastes in cement manufacturing, either as a

supplementary fuel or substitute for other raw materials, provides an option for simultaneously eliminating waste and recovering energy and materials [1,2]. This concept has been developed and used for co-processing problematic waste such as municipal solid waste (MSW), sewage sludge, persistent organic pollutants (POPs) waste, contaminated soil, and fly ash [3–8]. In Europe, most cement plants use wastes with high calorific values, i.e. waste-based/alternative fuels and raw materials, to substitute part of the primary fuel and the natural raw material. This substitution policy is acknowledged by the Stockholm Convention Best Available

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Techniques/Best Environmental Practices (BAT/BEP) guidance [9] and the Basel Convention technical guidelines [2].

Globally, cement kilns are increasingly being used for co-incineration of waste. Many developing and emerging countries have acquired initial experiences with state-of-the-art co-processing over the past 10 years [10]. Several emerging countries, including China, are also increasingly using cement kilns for co-processing not only waste such as sewage sludge [8] but also hazardous waste such as POPs [11,12] or fly ash [7]. The use of co-incineration with cement kiln is expected to further increase in developing countries where most waste is still being dumped [1].

Switzerland and Germany have been using waste-based raw materials and fuels since the 1970s and therefore have more than 40 years of experience in secondary materials use in cement kilns, including emission control and development of regulations. In 2018, these waste-based fuels accounted for around 67.5% of the required heat demand in Germany [13] and 65.5% in Switzerland [14]. Their experiences with controlling emissions and developing or adjusting regulatory frameworks might be of interest to developing countries in the early phases of developing a framework for co-incineration in cement kilns.

In 2000, the European Union regulated the co-incineration of waste [15]. This directive applies to all countries of the European Union. In addition, individual countries are able to enact more far-reaching provisions under their national law. Germany was already regulating the incineration or co-incineration of waste [16] before the European regulation took effect, including some much stricter provisions. Today, Germany is a trendsetter with regard to regulations on the co-incineration of waste in cement plants. Switzerland is not a member of the European Union and therefore does not have to adopt the European regulations. The country has its own legislation in this area, and in some cases its regulations differ significantly from the European and German ones.

There is often public debate regarding regulations on emissions of organic compounds because cement plants that use waste may emit higher levels of organic compounds than, for example, waste incineration plants. However, emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) from cement plants are normally low for cement kilns, with some exceptions [5,17], and are on average lower than from waste incinerators in particular in countries without PCDD/PCDF limits, as can be seen from the emission factors in the UNEP toolkit [18]. However, cement plants typically have higher total organic carbon (TOC) emissions than waste incinerators, particularly in industrial countries where regulations for waste incinerators exist. The exhaust gas concentrations of carbon monoxide (CO) and TOC are a measure for the combustion quality of the wastes utilized in waste incinerators and regulated in industrial countries. By contrast, clinker burning is a material conversion process and the emission of CO and organic compounds from the fuels occurs concurrently with the thermal decomposition of organic material from the raw material mixture of limestone, marl, shale, etc.

In this paper we present lessons learned from Germany and Switzerland on emissions of TOC, benzene, unintentional POPs (dioxins) and other pollutants, and discuss the root causes of the issues encountered. The good and bad experiences and practices of co-incineration of wastes in industrial countries can support policy making and control of co-incineration of wastes in developing countries.

2. Materials and methods

2.1. Standards used in plant measurement

The sampling and analysis were conducted according to

European or international standards:

The continuously measuring devices of the cement plants (CO, TOC, O₂, etc.) were used for investigations in the plants. These devices from different producers had to be certified according to EN 15267 [19]; calibrated annually according to EN14181 [20] and validated for these measurements, i.e. checked against a reference method. Other measurements inside the plants or in the laboratory were conducted according to the following international standards:

- DIN EN 15058 for CO [21].
- DIN EN 12619 for TOC Deutsches Institut für Normung [22].
- DIN EN 13649 for benzene [23].
- DIN EN 1948 for PCDD/PCDF [24].

2.2. Expulsion Test

The Expulsion Test was developed by Waltisberg [25] in Holcim and was therefore only available for Holcim group plants, but the method and idea behind the investigation was published in 1998 (Waltisberg, 1998) (see Fig. 1). Based on experiences from emission measurements in cement plants and theoretical studies, a laboratory test was developed that simulates the conditions under which raw materials are heated in a cement kiln. This test can predict the emissions from the raw materials. It was first used for projects developing new quarries or extending existing ones. However, it was soon recognized that the test was also suitable for assessing waste-based raw materials and splitting the emission fractions from the combustion process and from the raw materials.

A ground sample, e.g. a raw mixture or a raw material component, is heated from ambient temperature to approximately 750 °C in a small oven for a given time (Fig. 1), during which a constant volumetric flow of carrier gas flows through the sample. The carrier gas can be made in any required mixtures from pressure cylinders. The gaseous organic (and inorganic) compounds that are expelled are carried out of the heating zone with the carrier gas and are passed to measuring devices such as a special mass spectrometer or a flame ionization detector. (Fig. 1) The emission of the material in a cement kiln can be calculated based on these measurements.

The whole equipment of the Expulsion Test, including the control system, was designed and manufactured in-house. Mainly, the following analytical instruments were used:

- an AirSense mass spectrometer (V&F Analyse-und Messtechnik GmbH, 6067 Absam, Austria)
- a flame ionization detector 3–100 (J U M. Engineering GmbH, 85,757 Karlsfeld, Germany)

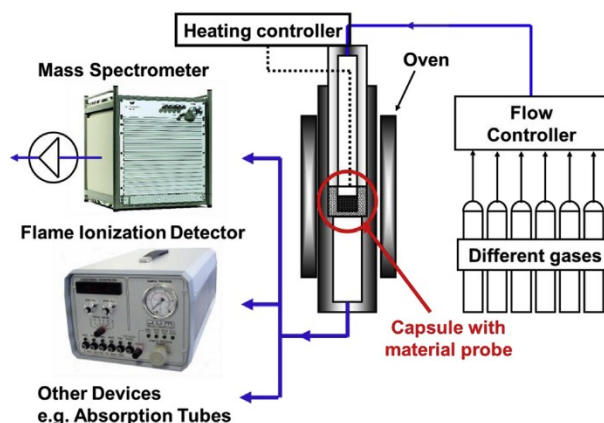


Fig. 1. Schematic of the Expulsion Test.

The devices used for this laboratory test were validated at regular intervals by using recognized reference methods, e.g. benzene with EN13649 [23].

3. Results and discussion

3.1. Limit values for major organic emissions in Germany and Switzerland

In all European countries, including Switzerland, emission values are stated as mass per cubic meter, subject to the following conditions:

- Normal conditions: 0 °C, 1013 mbar
- Dry exhaust gas
- Reference oxygen content of 10 vol-%

All limits given are daily averages.

3.1.1. Total organic carbon (TOC)

Germany defines in their 17th Ordinance for (co-)incineration of waste 17th BImSchV §8 a TOC limit value of 10 mg/m³ for waste incineration plants and cement plants (17th BImSchV, Annex 3, 2.1) (Table 1). The clinker burning process is not a pure combustion process but a material conversion process. Emissions occur both from the combustion and from the thermal decomposition of the organic components of the raw material, which also leads to raw material-related emissions of carbon monoxide and organic compounds. The legislature has taken this fact into account and has created an exemption (BImSchV, Annex 3, 2.2.1), which allows authorities to set higher TOC emission limit values for cement kilns if this is necessary due to the composition of the natural raw materials and if it can be ruled out that the waste incineration will not give rise to additional emissions. The word “natural” is important in this context. This exemption can only be applied if the additional emission comes from the natural components such as limestone, marl, clay, etc. and not from added secondary waste raw materials or the firing.

The challenge with this regulation and related exemption is determining the proportions of emissions from the combustion and from the raw materials. Up until the 1980^s there were still kilns with preheaters and without secondary firing and the TOC fractions from the main flame (explained later) were usually below, or even significantly below, 10 mg/m³. This is no longer the case. Most of today's preheater kilns have a secondary firing (kiln inlet or calciners) and it is extremely difficult, if not impossible, to determine the proportions of emissions in the process. Instead, the emissions would have to be determined by an Expulsion Test or an equivalent testing system.

The German TA [26] (TA [26]; Section 5.4.2.3) takes into account the possibility of emission of organic substances from raw materials contaminated with “relevant contents” of organic substances. According to the regulation, these substances shall be added to the kiln via the kiln inlet or to the calciner to destroy the organic content so that it is not released to the environment (TA [26]).

Switzerland used to have no limit value for TOC until 2016,

when it introduced a high limit value of 80 mg/m³ in the Ordinance on Air Pollution Control [27]; Annex 1, item 114) (Table 1). The Federal Office for the Environment [28] justifies the high level of this limit because “...contaminated soil can be used as a substitute for raw materials in all Swiss cement plants.”

Switzerland allows the use of wastes with problematic compounds as raw material substitutes if the organic substances do not exceed certain concentrations, e.g. 10 mg/kg for polychlorinated biphenyls (PCBs) [29]; Art. 24 and Annex 4, Number 1.1). The allowable waste quantities are limited by limits on the concentration of certain heavy metals in the clinker and by the provision that raw meal substitutes may not account for more than 5% by weight of the total quantity of raw material and raw meal correctives.

3.1.2. Benzene

In both countries benzene is classified as a carcinogenic substance and is limited to 5 mg/m³ (Table 1).

3.1.3. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs)

The emission of PCDD/PCDFs is regulated equally in Germany and Switzerland. Emissions of dioxins and furans, expressed as the sum of the toxic equivalents according to EN 1948–1, shall not exceed 0.1 ng/m³ (Table 1).

3.1.4. Carbon monoxide (CO)

In Germany, the 17th BImSchV [16]; Section 2.4) does not define a limit value for cement plants, but a limit value can be defined by the local authorities depending on the specific conditions of the cement plant.

In Switzerland, neither a continuous measurement nor a limit value for this pollutant is defined in the section of the Ordinance on Air Pollution Control for Cement Plants [27]; Annex 1, Number 119).

3.2. Feeding points for fuels and raw materials

In modern cement kilns with preheaters, fuels can be fed in at two points, namely into the main firing (main flame) and into the secondary firing (kiln inlet or calciner). The fuel distribution depends on the design of the kiln.

For preheater kilns without calciner, up to a maximum of 15–20% of the heat consumption can be fed to the kiln inlet. For preheater kilns with calciner and tertiary air, 40–60% of the heat consumption can be generated in the calciner. It is also possible to supply additional lumpy fuels up to approx. 10% directly to the kiln inlet, whereby the total input of the secondary firing (kiln inlet and calciner) must not exceed 40–60%.

Raw materials are fed into the preheater after the grinding and drying process.

In rare cases, (waste) raw material components are also fed directly into the kiln inlet. These are components that are contaminated by organic compounds (e.g. waste-based components) or natural components that would lead to high emissions. As shown in 3.3, such raw materials with high TOC emissions should be added at the end of the kiln (at approx. 1100 °C) so that the organic pollutants are destroyed and are not evaporated and

Table 1
Regulatory limits for TOC, benzene and PCDD/PCDF in Switzerland and Germany.

	Germany (D)	Switzerland (CH)	Notes
TOC	10 mg/m ³	80 mg/m ³	D: Derogation for high emissions from natural raw material
Benzene	5 mg/m ³	5 mg/m ³	
PCDD/PCDF	0.1 ng/m ³	0.1 ng/m ³	
CO	none	none	D: Limit value can be defined by local authorities

emitted during heating up in the preheater.

3.2.1. Maximum input of fuels

3.2.1.1. Main flame. In the area of the main flame the material is sintered to clinker. This requires a high temperature in the flame (peak temperature: approx. 2000 °C), as well as a fuel or fuel mixture with a high calorific value. Waste-based fuels often have medium or even low calorific values and therefore reduce the combustion temperature due to their water (moisture) content or their high ash content. The following values are given as guidelines for the maximum possible inputs of water and ash with which a sufficiently hot flame can still be produced in the rotary kiln (Table 2). The maximum water and ash input specified in the table cannot be cumulated.

3.2.1.2. Secondary firing (kiln inlet and calciner). In secondary firings, waste-based fuels are predominantly used in Germany and Switzerland, fed either directly into the kiln inlet or via a calciner. These fuels are mostly coarse-grained, even lumpy (e.g. tires), often inhomogeneous and can contain a lot of moisture and ash. The input of fuels into a secondary firing system is therefore limited, with the following approximate guidance values:

- Kilns without calciner, input to kiln inlet
 - Lumpy fuels (e.g. tires): maximum approx. 10–15% substitution related to the total heat consumption (primary and secondary firing) of the kiln;
 - Solids < 50 mm (e.g. plastic): maximum about 20% substitution;
- Kilns with cyclone preheater, calciner and tertiary air duct
 - Solids <50 mm: 30% substitution (approx. 50% of the heat requirement of the calciner);
 - Additional maximum 10% substitution by lumpy fuels fed to the kiln inlet;
 - Liquids: up to the maximum heat requirement of the calciner (40–50% of the total heat requirement of the kiln).

3.2.2. Inhomogeneity of the waste-based fuels

As previously mentioned, the fuels used are very often inhomogeneous. Particularly for waste-based fuels, the calorific value very often fluctuates as a result of inhomogeneous composition, agglomeration, etc. The required homogeneity of waste-based fuels, fed into the main or secondary flame, depends on the following factors:

- Short-term fluctuation of the calorific value (short-term = minutes);
- Short-term fluctuation of the mass flow into the kiln, which is determined by the quality of the fuel and the dosing system (short-term = minutes);
- Substitution rate of the waste-based fuel (part of the heat consumption of the kiln).

The combined influence of the first two factors leads to a variation of the heat input into the kiln system. In the case of higher fluctuations, effects due to inhomogeneity are to be expected (e.g. CO formation, increased heat consumption, reduced production

capacity, higher sulphur cycles, etc.).

The following rule of thumb applies:

Percent Variation of the Heat Input x Percent of Substitution < 100%

where:

$$\% \text{ Variation} \sim (\text{Maximum} - \text{Minimum}) / \text{Average (in \%)} \\ \% \text{ Variation Heat Input} = \text{Fluctuation Calorific Value} + \text{Fluctuation Mass Flow}$$

Example:

25% Substitution: < 4% Variation in Heat Input.

5% Substitution: < 20% Variation in Heat Input.

3.3. Source of organic emission of cement kilns from raw materials

Between 1993 and 2010, about 2000 samples were tested with the Expulsion Test. Approximately 2/3 of the samples were waste-based and the rest “natural” raw materials. It turned out that the behavior of the waste-based raw materials was in part significantly different from that of the “natural” materials (limestone, marl, slate, etc.), as will be shown below (see Fig. 1).

3.3.1. Organic emissions from “natural” raw materials

“Natural” raw materials (limestone, marl, shale, etc.) used for cement production contain varying concentrations of organic compounds, some of which are embedded in quite complicated structures in the raw material. If such a raw material or raw material mixture is heated in a preheater of a cement kiln then these organic constituents do not simply vaporize from the base material, but rather smaller compounds split off in the temperature range between 300 and 600 °C from degradation processes (“cracking”) and are then emitted at the chimney. This means, for example, that no benzene can be detected in the raw meal; it only develops when the material is heated [25]. Fig. 3 shows the development of different organic compounds from a raw meal. The approximate

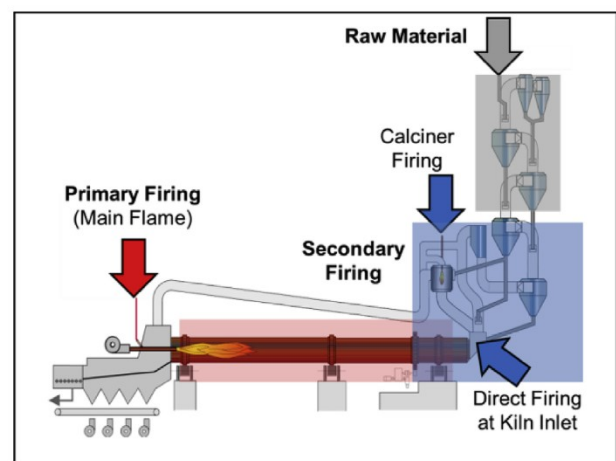


Fig. 2. Feeding points for organic compounds.

Table 2

Guidelines for maximum water and ash inputs.

Kiln Type	Water kg H ₂ O/t clinker	Ash kg ash/t clinker
Preheater kiln without calciner	0.10	0.35
Preheater kiln with calciner and tertiary air	0.05	0.15

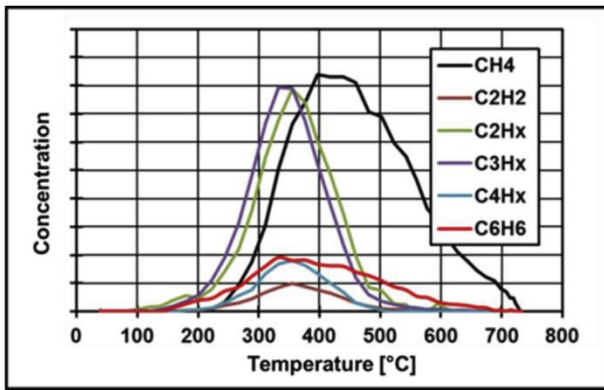


Fig. 3. Development of organic compounds from a raw meal investigated with the Expulsion Test.

Table 3
Emitted compounds.

Compound	% of TOC
Methane	20–40
C ₂ -Compounds	25–35
C ₃ -Compounds	20–30
C ₄ -Compounds	<6–8
Benzene	“low” to 8
BETX ^a	“low” to 12

^a Sum of Benzene, Ethylbenzene, Toluene and Xylene.

emissions of “natural” raw material mixtures or their individual components are listed in Table 3.

Trace amounts of naphthalene could also be detected in some measurements, with maximum emissions were in the range of 0.2–0.3 mg/m³. Other polyaromatic hydrocarbons or chlorinated hydrocarbons were not detected at all, i.e. they were not present or the concentrations were below the detection limit (<0.05 mg/m³).

Quarry investigations have shown that, depending on the mining area, changes in the average content of organic compounds and the organic emission can occur. If, however, mining takes place in a certain narrow area of the quarry, the content fluctuates relatively little (Fig. 4). Size changes in organic content may also occur when materials from different quarries or quarry layers are mixed together.

In one Swiss plant, marl from two layers was mixed with limestone. The upper marl layer emitted about three times the amount of the lower layer. The plant mixed different amounts of these two marls, depending on the quarry excavation phase. Since a

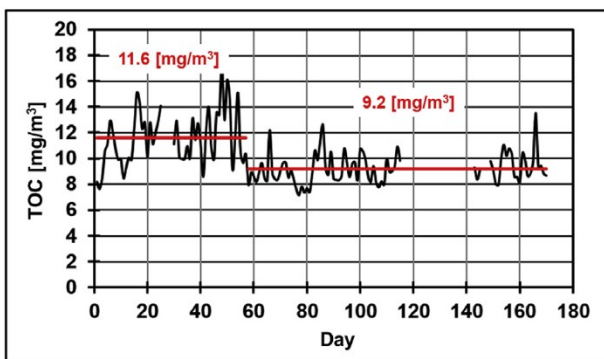


Fig. 4. TOC emissions from a cement kiln showing slight variations depending on the position of the raw material in the quarry.

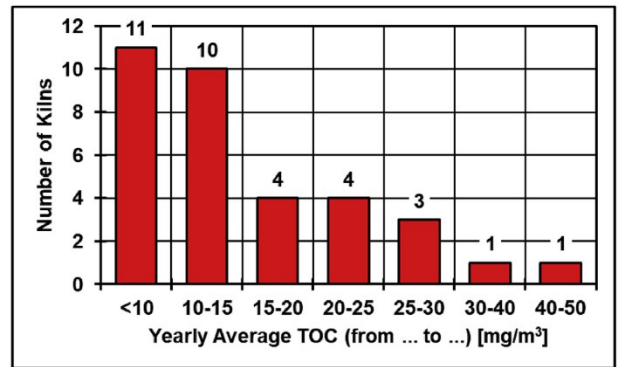


Fig. 5. TOC emissions from German cement plants in 2018 [13].

production quantity of about 10 days was always mixed with the limestone, different emission levels were measured among the individual mixing periods, but the emissions from the raw mixture fluctuated only slightly within the 10-day period.

About 600 probes from all over the world analyzed with the Expulsion Test [25] have shown that the TOC emissions from the “natural” raw materials mixtures range between negligible values to about 60–80 (mg/m³). Higher emissions were found in very few cases. In one instance, an emission over 3000 mg/m³ was calculated from the Expulsion Test and also confirmed by emission measurements in the plant.

Emissions from the raw material mixtures of the Swiss cement plants average between 20 and 35 mg/m³, but some of the individual components, mainly marl, which can have emissions of up to about 30–50 mg/m³. If, for some reason, more marl is used in the mixture, the emissions will exceed 20–35 mg/m³.

Samples from Germany showed similar organic emissions as the Swiss samples. However, the number of plants investigated is too small (5 out of approximately 40 plants) to give an average value for Germany. Also, in Germany there are probably quarries with a higher TOC emission.

The Association of German Cement Industry [13]; section 5.6) published the 2018 measured annual averages for the TOC (ΣC) in the clean gas from 34 rotary kiln plants. Fig. 5 shows the measured values, read from the VDZ publication, divided into emission classes (emission from/to).

The figure shows that the annual mean value at the majority of German cement plants exceeds the limit value of 10 mg/m³. If the daily mean values for which the limit value is defined could be taken (not available), the number of plants would be even higher.

In Germany, therefore, the vast majority of cement plants must make use of the regulatory exemption to exceed 10 mg/m³. The exemption, however, allows an increase in the limit value only if the increased emission is caused by the “natural” raw material. This is precisely where the major problem lays, namely in the separation of the raw material emission fractions from those of the fuel(s), especially waste-based fuels. This could be done for instance by determining the TOC emitted by the Expulsion Test or a similar test. Therefore to this day, the exemptions are granted without precise knowledge of the actual situation, because there is no recognized measurement method with which the individual emission shares can be determined. It is likely that higher emission values are not always caused by the “natural” raw material, but by the fuels or waste-based raw materials.

3.3.2. “Waste-based” raw materials and emissions

In contrast to “natural” raw materials, organic compounds in waste-based raw materials are usually only adsorbed in the base

Table 4
Some emission results from waste-based raw materials.

Investigated waste-based raw materials	Observed emissions
Contaminated soils	Very inhomogeneous; mostly structures of oils or gasoline; partly containing problematic chlorinated pollutants (PCBs; PCDD/PCDFs) or mercury; cyan compounds
Combined wastes from street cleaning, including from emptying street drains	BETX (benzene, ethylbenzene, toluene, xylene)
Foundry sand	Non-chlorinated furans
Iron correction components from chemical industry	Chlorinated benzenes
Lime hydrate (waste)	Acetylene and BETX
Fly ash from power plants	Benzene and phenol structures
Materials from chemical industries	BETX, chlorinated benzenes and phenols, polyaromatic hydrocarbons (PAHs), PCBs, etc.
Lining of electrolysis cells of aluminum smelting furnaces	Cyan compounds

material. Adsorption is the attachment of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. Therefore, the adsorbed organic compounds usually evaporate already at low temperatures, below 300 °C–500 °C in the preheater/cyclons, and are not oxidized. Importantly, they do not reach the temperature zone in the kiln system at which they could be destroyed.

This behavior is characteristic of many organic compounds studied with the Expulsion Test [25], which have either been used or tested for a possible use in cement plants. Table 4 summarizes the results of some of the tests, which concern the behavior of the individual investigated samples tested and are not transferable to all other samples of the same waste-based raw material category. For example, other samples of iron correction components showed very small and above all no critical emissions.

Germany takes into account the possibility of emission of organic substances from raw materials contaminated with relevant content of organic constituents and specifies that these materials should be added to the kiln inlet or to the calciner (see Fig. 2). The critical point is the definition of “relevant content” in contaminated raw materials. This expression can be interpreted very differently by the authorities with regard to the substances covered and their concentrations. A negative example of such an interpretation and regulatory decision is certainly the “Körtschitztal case” in Austria (see section 3.3.2 below).

Unlike Germany, Switzerland allows the use of waste raw materials with hazardous compounds as a substitute for raw materials, even up to a PCB content of 10 mg/kg (see 2.1.2). The authors consider this Swiss ordinance [29] to be very dangerous and have already shared their concerns with the Swiss government, without success so far.

3.3.2.1. Case studies of halogenated aromatic emissions from waste raw materials

3.3.2.1.1. Monochlorobenzene (C_6H_5Cl). During an annual review of the organic emissions of a cement plant the compound monochlorobenzene (C_6H_5Cl) was measured in the exhaust gas. The Expulsion Test performed on the raw meal and on the iron correction component (waste from the chemical industry) showed an expulsion of monochlorobenzene from the used iron correction component and of phenol in the temperature range between 200 and about 600 °C (Fig. 6). A later chemical analysis from the supplier, a chemical manufacturer, confirmed this finding.

In this case, for example, the monochlorobenzene was already evaporated from the iron correction component at relatively low temperatures in the raw meal mill or in the upper cyclone stages. The two components were therefore not oxidized because the temperature was too low, but the aromatic pollutants were emitted at the chimney.

3.3.2.1.2. Hexachlorobenzene (HCB) emission and pollution from HCB-waste destruction. In March 2014, the Austrian Agency for

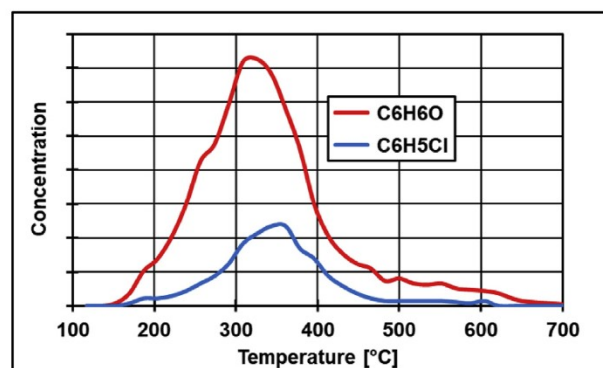


Fig. 6. Expulsion Test with iron correction component.

Health and Food Safety found hexachlorobenzene (HCB, which is a POP) in foods (milk products and meat) from the Görtschitztal at levels exceeding the food limit [30,31]. The contamination originated from the disposal of blue lime contaminated with HCB in a cement kiln. The HCB-contaminated blue lime came from the landfill of an organochlorine company (Donau Chemie). Between 1952 and 1981, blue lime ($Ca(OH)_2$), a byproduct of acetylene production, was disposed together with HCB and other chlorinated hydrocarbon-containing sludges from organochlorine solvent production in a landfill of Donau Chemie in the municipality of Brückl im Görtschitztal, Austria [30–33]. Within the scope of the remediation of the landfill carried out from 2011 onwards, a cement plant was awarded a contract for the thermal disposal of the material after a public tender. According to the Donau Chemie, the waste material supplier, high temperatures above 800 °C were needed for disposal.

A report of the state authority of Carinthia (Kärnten) [30,31] revealed that 95% of the POPs were fed into the raw mill. The published facts and figures further prove that in this case ignorance of the cement process probably led to these problems.

1. The HCB is only slightly bound in the basic material blue lime and has a boiling point between 323 and 326 °C. Given its relative low boiling point, the compound evaporates from the blue lime in the raw meal mill or in the uppermost stage of the preheater.
2. While the mill was running (so-called compound operation), a large part of the compound was adsorbed on the raw meal and returned to the process. A circuit was therefore established for HCB between the upper cyclone stages and the filter system in the compound mode. In our experience, such cycles also build up in cement plants for other compounds with similar persistence and boiling points, e.g. PCBs and PCDD/PCDFs.

3. When the mill was stopped (so-called direct operation), the adsorption was much smaller and high quantities of HCB were emitted.

The published measurements and estimates proved the evaporation process described above. 100,000 t of blue lime waste containing 430–750 kg of HCB was fed into the cement kiln and it was estimated that 170–310 kg HCB (worst case 500 kg HCB) was desorbed and released to the environment over a period of 10–13 months [30,31]. On December 16, 2014, the state government withdrew its approval for the recycling/disposal of HCB contaminated blue lime at the cement factory and cement production was resumed without the use of blue lime on February 13, 2015.

The case of Görtscitztal demonstrates an essential fact: the organic compounds found in alternative raw material components, which are transported via the raw material path into the kiln system, evaporate during the heating process and are not oxidized or destroyed to a large extent, but a large proportion of them is finally emitted at the chimney. This case study also shows that although the cement kiln can destroy HCB if fed at the kiln inlet at 1100 °C, if operators lack a basic understanding of the process and chemistry involved they will likely select the easiest and cheapest feeding point namely the raw material path.

A governmental commission identified failures made by the cement company, the competent authority, experts and surveyors [32]. The case study highlights that despite the technical capability of a plant to destroy waste, the company needs educated personnel who understand the process and can select the right feeding point.

The competent authority also failed to request monitoring for HCB during the full scale destruction process [32], because no HCB emissions were detected during the pilot testing. However, during that test the appropriate high temperature feeding point was used. Therefore, full scale POPs destruction tests for all types of technologies require robust monitoring [34]. For POPs destruction in incinerators, cement kilns and similar facilities with direct emission to air, continuous sampling of the respective POPs and of PCDD/PCDFs should be required [34,35].

3.4. Influence of the firing on emissions

3.4.1. Main firing

A temperature of 1450 °C is required for sintering the raw material into clinker. The heat (radiant heat) is supplied by a flame with a maximum temperature of approx. 2000 °C. In the rotating part of the kiln, the gas remains at a temperature above 1100 °C for at least 5–8 s and, due to the clinker quality, combustion in the sintering zone of the rotary kiln must also be carried out with excess air. These are optimal conditions for the oxidation of organic compounds. Our measurements at the kiln inlet (transition section rotary kiln/pre-heater) at several kilns have shown that all organic substances of the main flame were oxidized and no organic compounds, in particular no chlorinated organic compounds, could be detected.

3.4.2. Secondary firing

Investigations with the Expulsion Test have shown that little carbon monoxide is produced from the raw materials of the cement plants. With a few exceptions, the maximum concentration from the raw material mixtures is about 500 mg/m³. The evaluation of the annual average values of carbon monoxide emissions in Germany in 2018 [13]; Section 5.6) shows that some cement plants have to significantly exceed this value (Fig. 7). It should also be noted that these are annual averages of the individual plants. Short-term emissions (e.g. daily average) may be significantly higher in some cases. Some of these pollutant emissions must therefore originate from combustion, probably mainly from secondary firing.

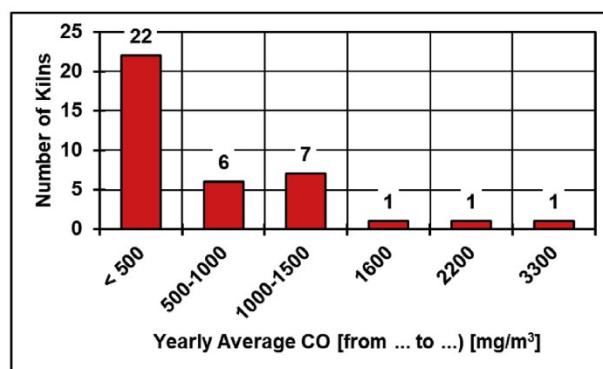


Fig. 7. CO emissions from German cement plants 2018 (data [13]).

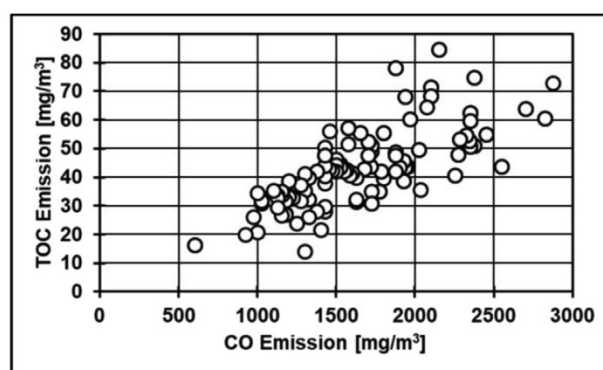


Fig. 8. Emission measurement in a cement plant with tire firing at kiln Inlet.

The daily mean values of individual German cement plants from 2008 to 2010 were evaluated by Schönberger and Waltisberg [36]. The analyses showed that in some plants the input to the secondary firing was probably too high or the fluctuation too high.

Figure shows such an example. In this plant tires are burned and the 5-day averages show very high CO and TOC emissions as well as a wide range of fluctuation. Such a behavior of the emissions can in no case have its cause in emissions from the raw materials. Here, tires are burned under reducing conditions with related CO and TOC emissions.

3.4.2.1. Secondary firing - direct firing at kiln inlet. In one of the first combustions of tires in a German cement plant, in the mid-1980s, it was found that carbon monoxide emissions changed significantly with the number of tires, specifically with the proportion of tires to the heat requirement of the kiln (Fig. 9). In particular, the tires led to a considerable increase in carbon monoxide emissions over about 15–20% of the heat requirement of the kiln. An increase in emissions of organically bound carbon (TOC) and benzene was also suspected, but a TOC measuring device was not available during the test. The researchers decided to make two short measurements of benzene emission with carbon tubes (absorption of a partial gas stream of activated carbon), which confirmed their suspicion. The benzene emission, which was later measured more precisely, was between 2.5 and 3.5 mg/m³ with little (<15% of heat consumption) or no tire input. The benzene did not originate from the tires but from the raw materials, as later investigations have shown. The emission, however, increased when tires fed at kiln inlet contributed 20% of the heat consumption to about 4.5–5.5 mg/m³ and therefore at or above the 5 mg/m³ regulatory limits in Germany or Switzerland (see Fig. 9)

In a later experiment in another cement plant, the problem of tire input into the kiln inlet was investigated. One short experiment

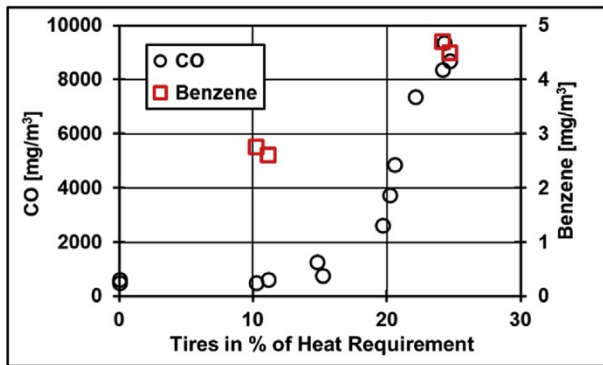


Fig. 9. Emissions of CO (average of approx. 8 h) and benzene (spot measurement) versus the share of tire combustion from total heat requirement.

investigated “overfeeding” with tires, i.e. too many tires were fed at short notice. The signals were continuously recorded with a special mass spectrometer. During normal operation (marked with number 1), no additional emissions from the secondary firing system were detected (Fig. 10). The measured organic emissions came from the raw materials. In the “overfeeding period” with tires (marked with the number 2), the organic components methane and benzene in particular rose sharply. Other components (e.g. C_2 , C_3 compounds) increased only insignificantly.

Similar tests in other plants with other wastes showed that material-specific compounds, such as benzene and styrene, increased with the addition of polystyrene wastes.

3.4.2.2. Secondary firing - calciner firing. The calciner is particularly suitable for the addition of waste-based fuels, which are evenly coarse-grained and contain a lot of ash and water (see 3.2.1). Very often these materials are also inhomogeneous.

In calciners, the so-called technique of staged combustion is most commonly used for the partial reduction of nitrogen monoxide from the rotary part. In a combustion zone after the rotating part, part of the fuel is burned under air deficiency, i.e. under reducing conditions. The nitrogen monoxide (NO) reacts with the carbon monoxide (CO) to form molar nitrogen (N_2) and water vapor (H_2O). Subsequently, the carbon monoxide is oxidized in a post-combustion zone. However, this post-oxidation requires sufficient air, which must be available in the right place, with the right fuel distribution and amount, etc. This is not the case in many calciners, and as a consequence carbon monoxide and other organic compounds are emitted from the calciner firing.

In a cement plant, about 50% of the heat consumption was generated in the calciner with coal. From the raw material analysis

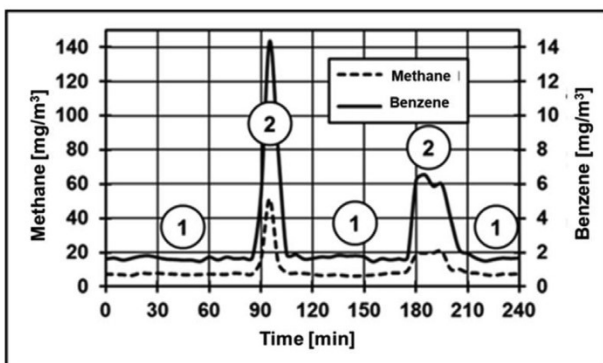


Fig. 10. Overfeeding test with addition of tires (2) compared to normal operation (1).

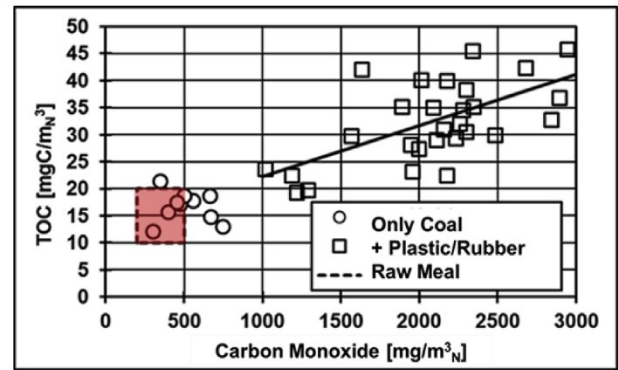


Fig. 11. Comparison of TOC and CO emission on a calciner firing with rubber and plastic addition compared to pure coal combustion.

with the Expulsion Test [25], the following emissions were predicted (see the dotted square in Fig. 11):

- CO: $350 \pm 150 \text{ mg/m}^3$
- TOC: $15 \pm 5 \text{ mg/m}^3$

When operating with coal, the emissions were measured (the circles in Fig. 11 represent the daily emission averages). Then, part of the coal, which accounted for about 30% of the heat consumption of the kiln, was replaced with plastic and rubber chips, and emissions increased significantly (see the squares in Fig. 11). One problem was that the plastic waste supply was not constant and blockages occurred repeatedly. In addition, the calorific value of the mixture fluctuated widely as a result of the partly inhomogeneous mixture.

The feed was improved and a better, more homogeneous mixture was used later. Unfortunately, there are no data available, but the plant reported that the CO emission could be stabilized at around $1000\text{--}1500 \text{ mg/m}^3$ and TOC emissions at around 25 mg/m^3 .

3.4.2.3. Increase of the limit value. Too high inputs or inhomogeneous waste-based fuels often increases the carbon monoxide emissions, which also reflects an increase of organic emissions (Figs. 8 and 11). Both emissions should be limited. As a general rule, the observed increased emissions are mostly of fuel-specific organic compounds, e.g. benzene from excessive tire combustion.

According to German regulations, the limit value for TOC emissions may only be increased if the proportion emitted in excess of the value of 10 mg/m^3 originates from “natural” raw materials. This is certainly not the case for the examples in Figs. 8, 9 and 11 and the limit value should not be increased here, but the plant should be required to improve the combustion quality.

The whole problem is played down in Germany. The VDZ sees the main cause for the excess CO and TOC emissions of the 2018 published environmental data in the raw materials [13]; Section 5.6). The problem of secondary firing is only mentioned in a short sentence, which discusses only TOC emissions and not CO emissions.

In 2016, Switzerland defined the TOC limit value in the Ordinance on Air Pollution Control as 80 mg/m^3 and does not restrict the cause of these emissions. It also does not consider whether the emissions originate from waste-based raw materials or fuels. It even officially allows the use of contaminated soil. This will lead to unnecessary releases to the environment and increased exposures around cement kilns evaporating POPs such as PCBs, HCB or PAH from contaminated soils, with potential risks to meat, milk and cheese production from cattle raised in the vicinity of such cement

kilns [32,37,38]. The case of the HCB contamination from an Austrian cement kiln (section 3.3) should be taken as a warning. It led to the pollution of approx. 300 farms, including milk and meat, and elevated HCB levels in humans [30–32].

3.5. Formation and release of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDFs)

Due to the regulatory and toxicological relevance of the PCDD/PCDFs, a short chapter on PCDD/PCDF formation and release from cement plants is described here.

3.5.1. Formation of PCDD/PCDFs in cement kilns

As illustrated by the investigations in cement plants, the problem in all cases was not the combustion, as VDZ [13]; 6.7) also emphasizes, but the addition of critical components to the raw material. This means that the cause of high PCDD/PCDF emissions can be found mainly in the components of the raw material.

As mentioned above, problematic compounds can be present in waste-based raw material components. The critical organic compounds evaporate below about 300–500 °C, are released from the preheater to the exhaust gas, are partly adsorbed again at the fresh raw material in the mill and are returned to the system (PCDD/PCDF cycle between upper cyclone stages and filter). When the raw mill is shut down, there is a much smaller absorption capacity on the kiln dust (the fresh raw material from the stopped-mill is missing), and a large part of the PCDD/PCDFs is therefore emitted (Figs. 12 and 13). A kind of “de novo synthesis” takes place in this critical

temperature range in the preheater, mainly because of the presence of precursors that originate from the waste-based components of the raw material.

The Swiss regulations fail to consider this major PCDD/PCDF formation mechanism and allow even PCBs, which are excellent PCDF precursors [34,39], in the raw material added to the raw mill (up to 10 mg/kg), thus eventually leading to PCB and PCDD/PCDF emissions.

3.5.2. Selected PCDD/PCDF problems and solutions for cement plants

In the literature, (e.g. Ref. [13]; Section 6.7), one often finds the statement that PCDD/PCDFs are only present in very low concentrations in exhaust gases from cement kilns. This statement is broadly valid, but there are exceptions with emissions of more than 100 ng Dioxin toxic equivalency (TEQ)/m³ [5,9]. The environmental data published annually by the VDZ also show that almost every year from 2002 to 2018 there is at least one measured PCDD/PCDF value close to, or even exceeding the limit value of 0.1 ng TEQ/m³. However, not much is known about the cause of these outliers.

In Switzerland, emissions exceeding the regulatory limit were measured in one plant between 2015 and 2018 (Fig. 12). There have already been problems in this specific Swiss plant since the late 90s (Fig. 13). Various dioxin measurements were carried out in this plant and the values were always well below the limit of 0.1 ng TEQ/m³, usually <0.01 ng TEQ/m³. Then suddenly high dioxin values between approx. 0.2 and 0.3 ng TEQ/m³ exceeding the regulatory limit were measured at this plant (Fig. 13). This occurred right after the plant burned waste oil and had to clean the waste oil tank. Part of the sludge from the tank was incorrectly fed into the mixed bed, i.e. to the raw material, and therefore introduced via the preheater. Since a baseline measurement for a test with plastic incineration was carried out at this time, the high dioxin values were measured and the cause – the addition of the oil sludge in the mixed bed – could be determined. The PCDD/PCDFs had accumulated in the system and the kiln dust. To clean the kiln at that time, a temporary device was installed with which the kiln dust was fed directly into the kiln inlet, i.e. into a very hot temperature zone to destroy the PCDD/PCDFs. This approach reduced the PCDD/PCDF levels significantly within a few days, returning to the “normal values” below about 0.005 ng TEQ/m³ after about 14 days (Fig. 13). A later analysis of similar oil sludge showed a high content of polychlorinated biphenyls and chlorinated organic compounds. The addition of contaminated raw material onto the mixed bed was also confirmed as the PCDD/PCDF source in other “dioxin cases” in other kilns and helped to eliminate corresponding errors.

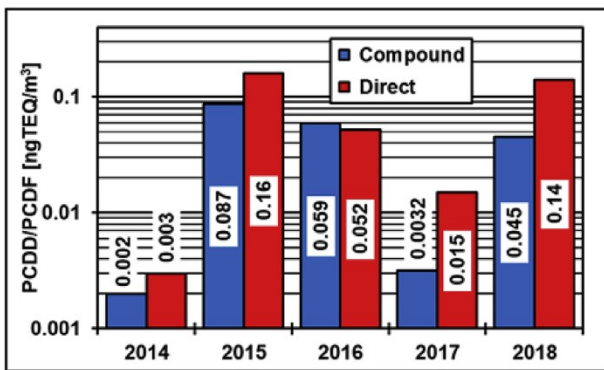


Fig. 12. PCDD/PCDF measurement in a Swiss plant (note: logarithmic scales).

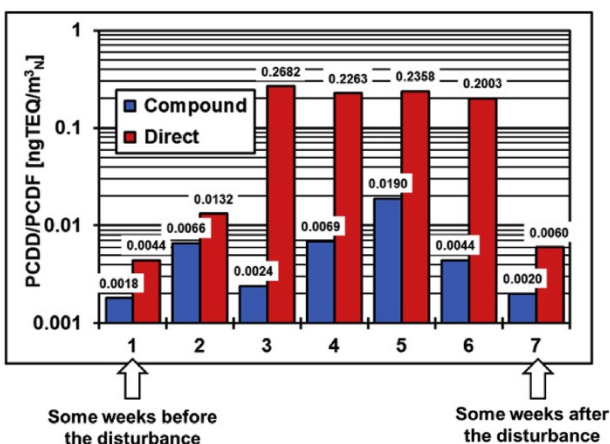


Fig. 13. Dioxin case study in a Swiss cement plant.

4. Conclusion

The co-incineration of waste in cement kilns is a viable waste management option and can solve some of the waste management problems of developing countries. However, co-incineration of waste can also lead to higher levels of hazardous emission if the operation is not appropriately controlled. This paper compiles information on problematic organic emissions from cement kilns. It highlights that waste-based raw material containing persistent organics such as PCBs, HCB, PCDD/PCDFs or PAHs should not be allowed to be added to the raw material or calciner since these compounds are just desorbed and emitted into the environment. Strict regulations that prohibit such practice are needed.

The TOC emission potential of the raw material can be assessed using the Expulsion Test described here and in Waltisberg [25]. By applying such tests, the emissions from the fuels, including from waste-based fuels, can be determined, restricted and controlled. The TOC emissions from natural materials cannot be avoided.

However, Switzerland recently implemented a high TOC limit value of 80 mg/m³ for cement kilns independent of the source of organic emissions. This TOC limit is too high and can result in unnecessary emissions of carcinogenic benzene and other pollutants. Furthermore the regulation is allowing even the use of PCB-contaminated soils as raw material (up to 10 mg/kg) which result in emissions of these PCBs and the formation and emission of PCDFs. The current regulation in Switzerland fails to restrict these avoidable hazardous pollutants. Also, the current TOC emission limit of 80 mg/m³ is far too high, given that the release from natural raw materials is on average between 20 and 35 mg/m³.

Organic compounds of waste-based raw material components can contain hazardous pollutants like PCBs and other POPs, which desorb if they are introduced via the raw mill or preheater and are released to the environment. Therefore, waste raw materials such as soils contaminated with POPs or other semivolatile toxic chemicals cannot be introduced via the preheater but need to be fed in the kiln inlet. Cement kilns treating POPs or raw material with problematic semivolatile organics need strict control and possibly continuous emission monitoring to avoid large environmental and human contamination such as in the recent HCB case in Austria.

Overall, more capacity building is needed globally on co-incineration of waste and the associated opportunities and risks. Within a cooperation project, Holcim and GIZ (former GTZ) have developed guidelines for co-processing waste in cement kilns that were and can be used for capacity building [40]. More projects like this are needed to educate the competent authorities and companies, NGOs and the public.

Declaration of competing of interest

None.

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