Formation and Emission Control of Organic Compounds and Carbon Monoxide in Cement Plants, especially when Co-Incinerating Waste

Workshop: Organic Pollutants Emission Control for Co-incineration in Cement Kilns

Tsinghua University, Beijing, China, 12.09.2019

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I. Introduction

- Cement plants that use waste generally have higher emission limit values than other plants that use waste, e.g. waste incineration plants. This leads to discussions and a lack of understanding among the population.

- The problem is that emissions from raw materials (limestone, marl, clay, etc.) overlap the emissions from incineration.

  In the German 17th BImSchV the limit value for large combustion plants of 10 [mg/m^3] was adopted, but an exception was created for cement works.

  > *The competent authorities can approve exemptions for sulfur dioxide and total carbon (note: this refers to TOC emissions) at the request of the operator, provided that these exemptions are necessary due to the composition of the raw materials and it can be ruled out that additional emissions of total carbon dioxide and sulfur dioxide ... result from the incineration of waste.*

Introduction

The organic emissions from cement plants are largely attributed to organic compounds in the raw material.

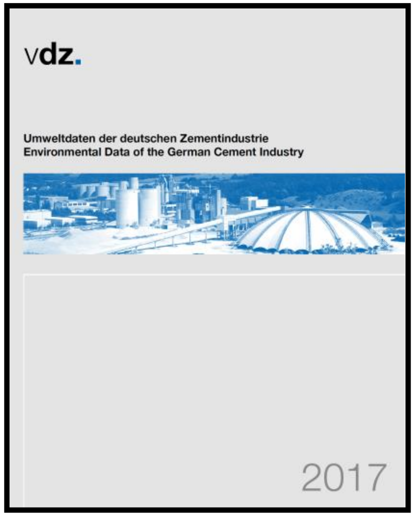
Fuels do not seem to play a role.

Examples VDZ:

- **TOC** (Total Organic Carbon): The emission of organically bound carbon during the clinker burning process are caused by the small quantities of organic constituents input via the natural raw materials (remnants of organisms and plants incorporated in the rock in the course of geological history). These are converted during kiln feed preheating and become oxidized to form CO and CO_2.
- **PAH** (Polycyclic Aromatic Hydrocarbons): The rotary kiln systems of the cement industry guarantee a virtually complete destruction of the PAHs input via fuels. Emissions are caused by organic constituents in the raw material.

Remark: The German Cement Industry publishes the measured emissions of all German cement plants every year (see VDZ, Environmental Data of the German Cement Industry)

In Europe it is the most comprehensive publication of environmental data. Other countries limit themselves to selected pollutants, e.g. NOx (Switzerland).



vdz.

Umweltdaten der deutschen Zementindustrie
Environmental Data of the German Cement Industry

2017

Some Definitions

- Alternative fuels also called secondary or waste-based fuels
  are substances that are suitable for replacing standard fuels (coal, oil, gas)
  e.g. tires, rubber, plastic, solvents, …
- Alternative Raw Materials also called secondary or waste-based raw materials are substances suitable for replacing natural raw materials (limestone, marl, shale), e.g. contaminated soils, filter materials, foundry sand, …
- Emission units:
  Emitted pollutants are indicated as emitted mass (milligram [mg], microgram [mg] or nanogram [ng]) per normal volume [m^3_N] (1013 [mbar], 0 [°C]) in dry gas condition and at a reference oxygen content of 10 [%]

II. Cement Process

Dudfield / South Africa

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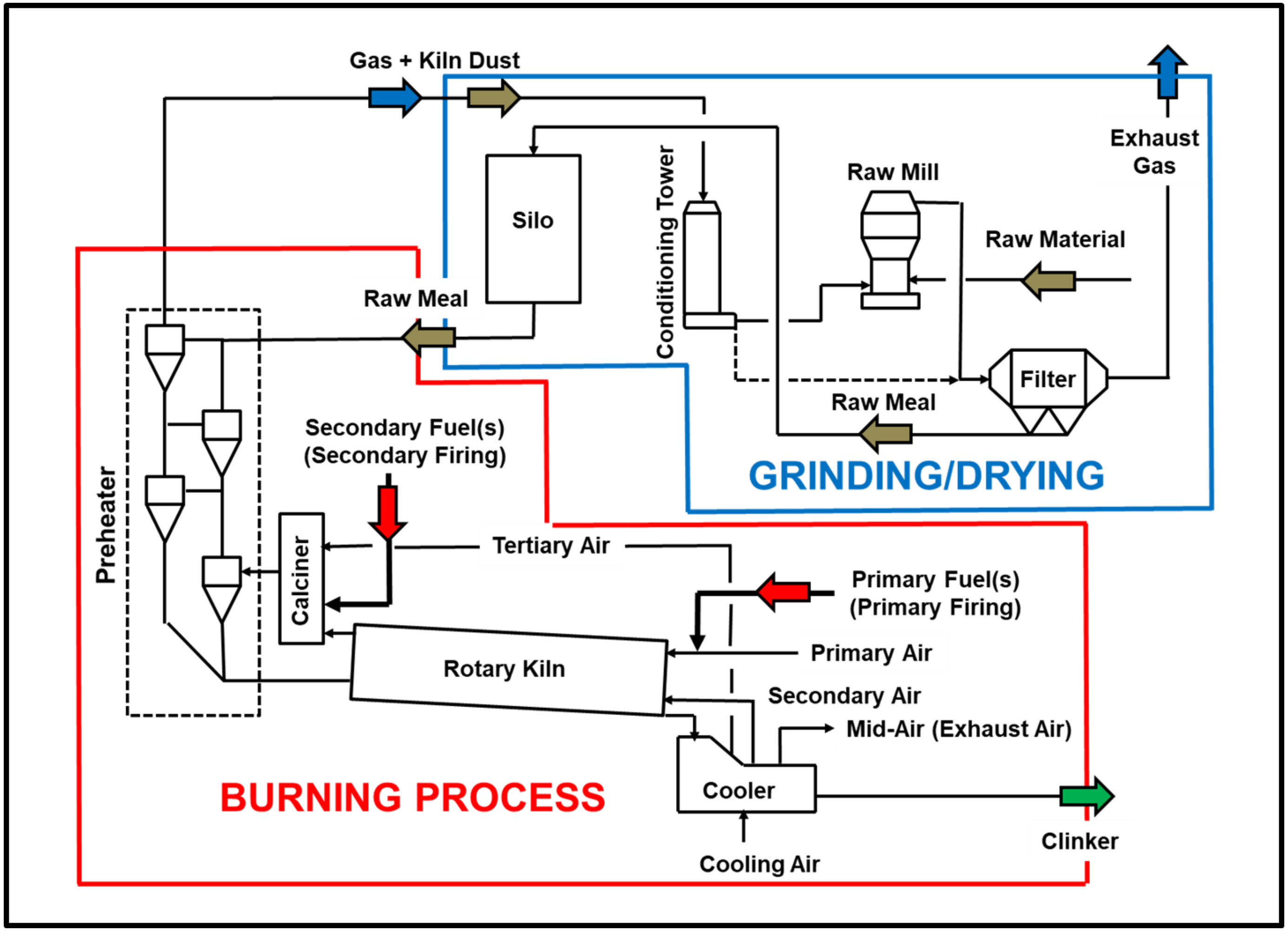
The Clinker Burning Process

The Clinker Burning Process can be divided into two sub-processes, namely the **Burning Process** and the **Grinding / Drying Process**



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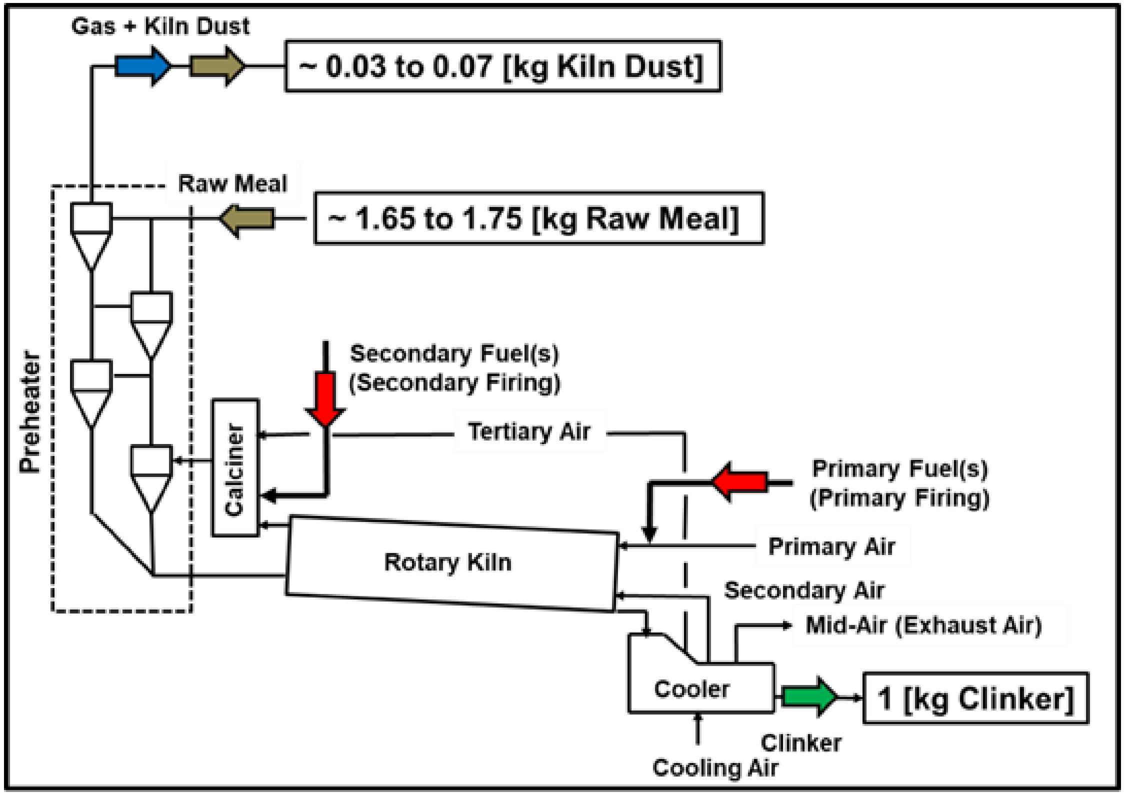
The Burning Process

- The Burning Process is operated **continuously**
    - Constant Input of Raw Meal from the Grinding/Drying Process)
    - Constant Output of Clinker
    - Constant Output of Kiln Dust to the Grinding/Drying Process)

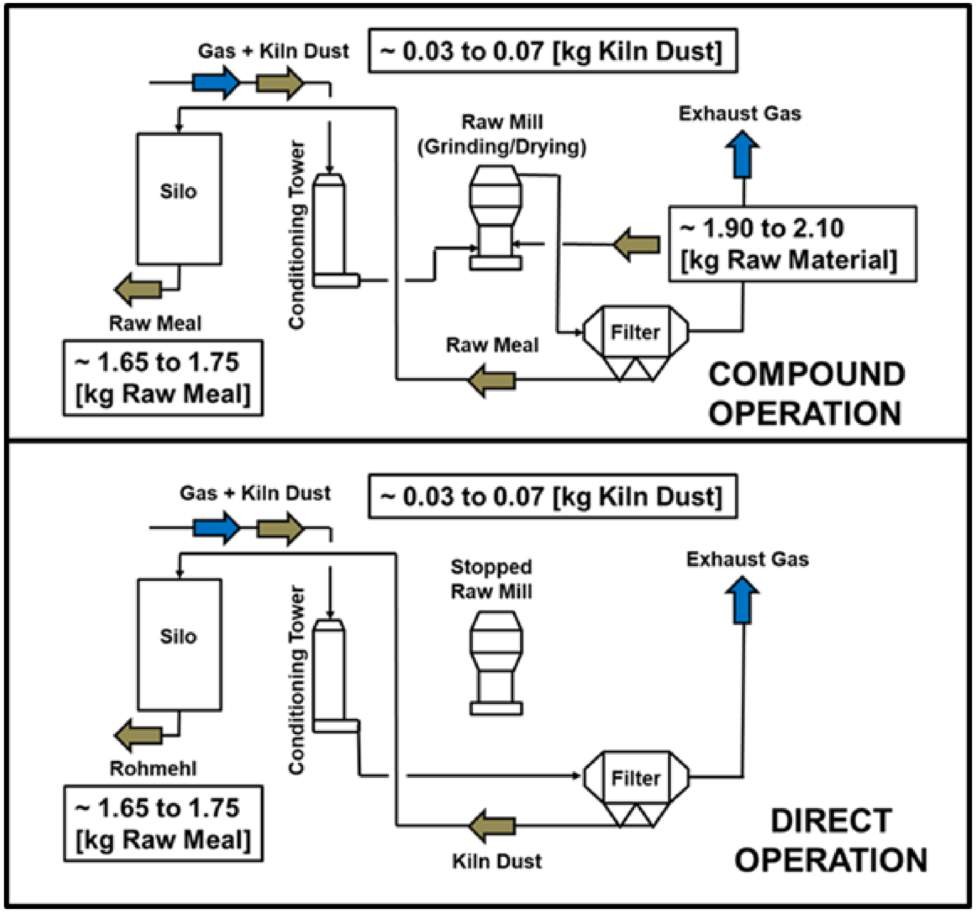
- Two Input Points of Fuels



The Grinding/Drying Process

The Grinding/Drying process is operated in two different modes, namely

- in compound operation (running raw mill) and
- in direct operation mode (stopped raw mill)



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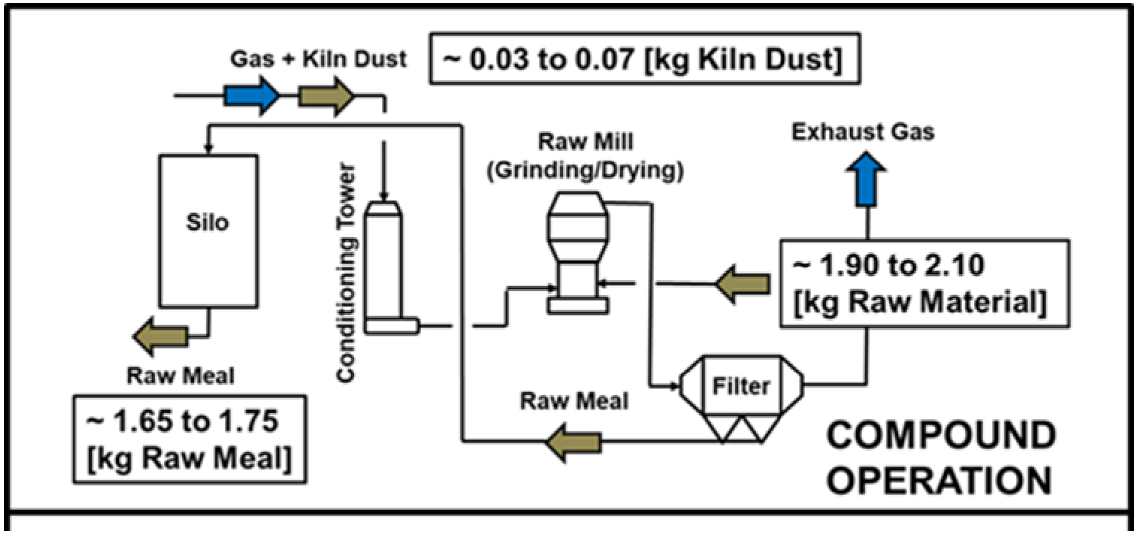
Grinding/Drying Process – Compound Operation

- About 80 to more than 90 [%] of the production time
- The raw material is ground on the one hand and on the other hand dried with the gas from the kiln system.
- Since 10 to 20 [%] of the time the raw mill is stopped, their capacity must be correspondingly slightly higher than the mass required by the combustion process of about 1.65 to 1.75 [kg raw meal].
- The temperature after the filter system, i.e. when entering the chimney, usually the ranges are between about 100 and 130 [° C].

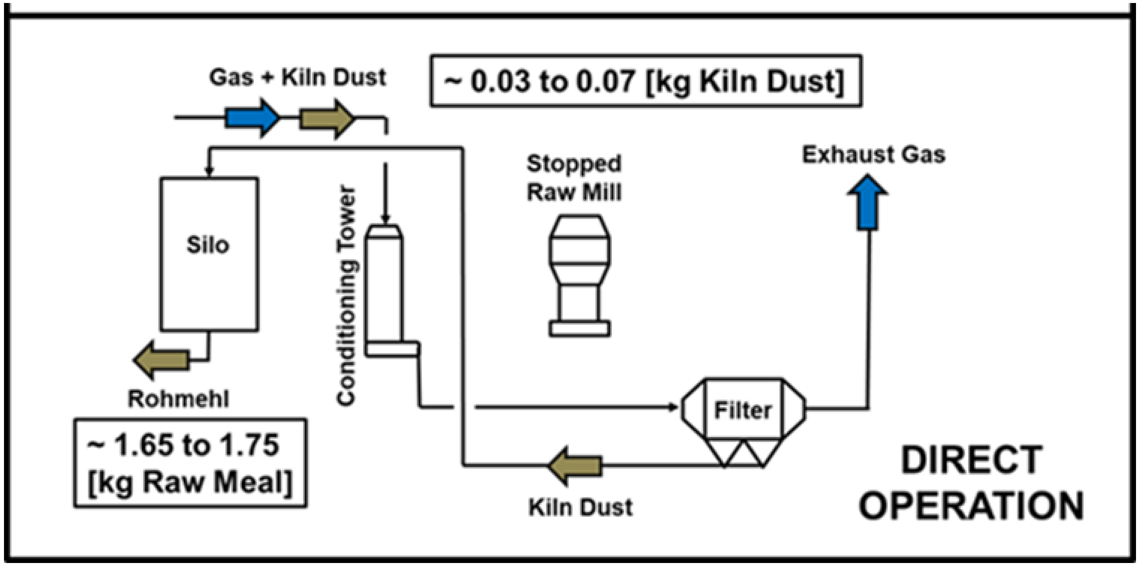
→ **High Mass Flow of Solids and Low Temperature**



Grinding/Drying Process – Direct Operation

- The Raw Mill is turned off and the raw meal is taken from the silo.
- The kiln gas and the kiln dust from the preheater are cooled in the conditioning tower (water injection) and then go directly into the filter.
- Filter:
  - As a solid, only the kiln dust is present (low mass flow)
  - The temperature after the filter, i.e. when entering the chimney, is higher than in compound operation and is at 150 [° C] or slightly higher.

→ Very Low Mass Flow of Solids and High Temperature



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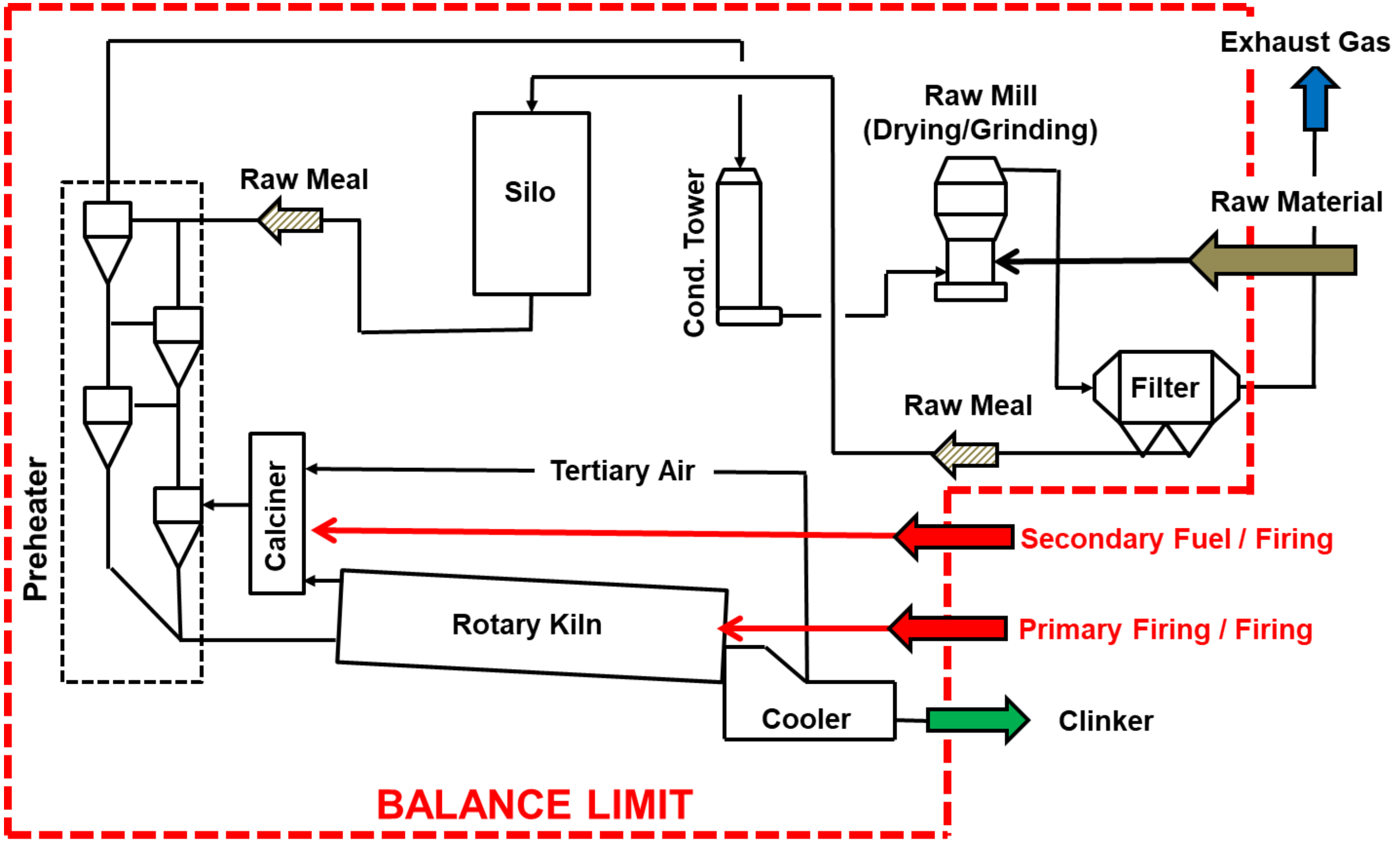
Wrong Investigation Method

«Black Box Method»

BLACK BOX

Difference = Input – Output

Difference = (Primary Fuel + Secondary Fuel + Raw Material)
– (Exhaust Gas + Clinker)



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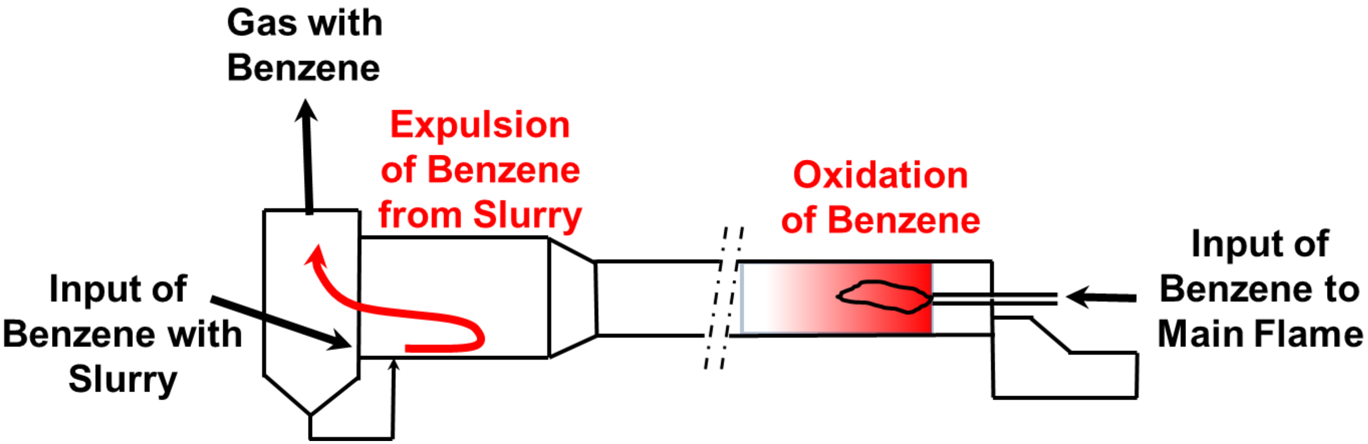
Result from a «Black-Bock» Investigation

Investigation

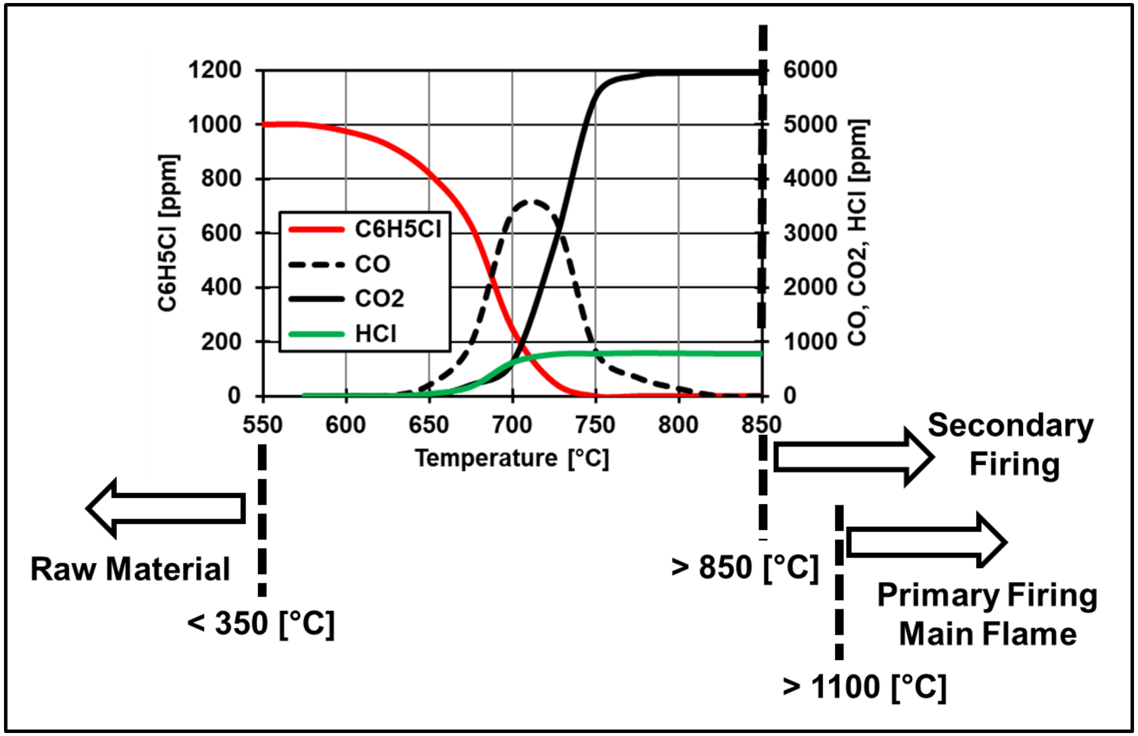
- Addition of benzene to the main flame of a wet process (80ties)
- No benzene was found in the raw material (sludge).
- Measurement of input (fuel) and output (exhaust gas)
- Result: Result: **No reduction but formation of benzene in the cement process from the fuels**

Reality

- Oxidation of additional benzene from the fuel
- Expulsion of benzene from slurry
  The analysis method (JW's Expulsion Test) was not yet known at that time.

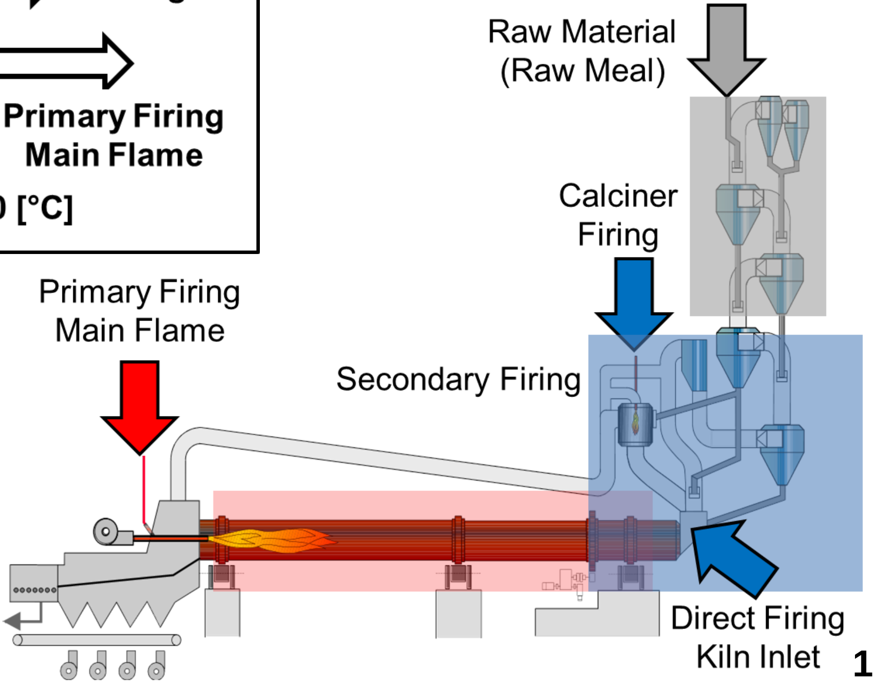


III. The Input-Points of Organic Compounds



Example: Input of Monochlorobenzene C_6H_5Cl

- **Input via Fuels**:
  Thermal degradation depending on conditions
- **Input via Raw Material**
  No thermal degradation (Evaporation)



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IV. The Impact of the Raw Material on Organic Emissions

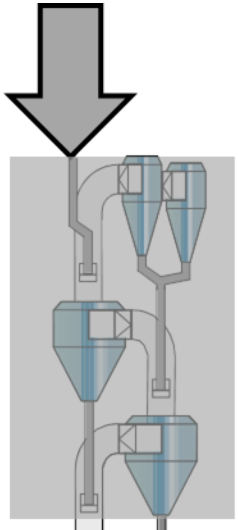
«Natural Raw Materials»
Limestone, marl, shale, …

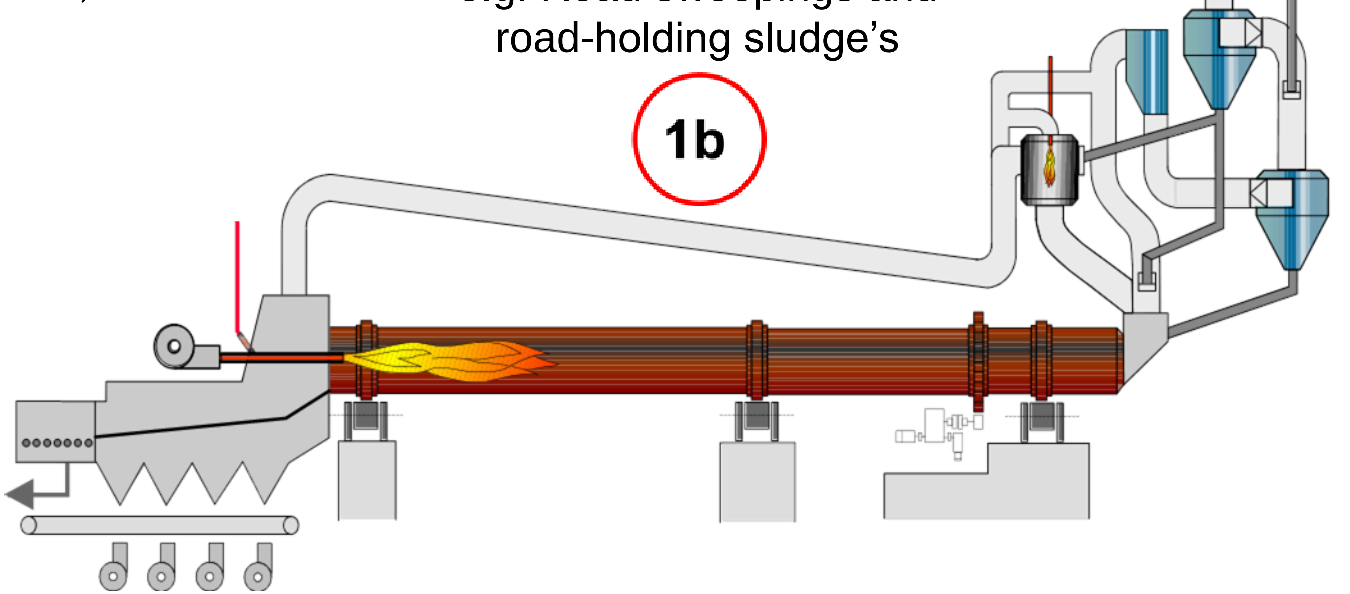
1a

1

«Alternative Raw Materials»
e.g. Road sweepings and road-holding sludge’s

1b





«Natural Raw Materials»

1a Limestone, marl, shale, …

Quarry of Holcim Siggenthal (Switzerland)

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Expulsion from «Natural Raw Materials»

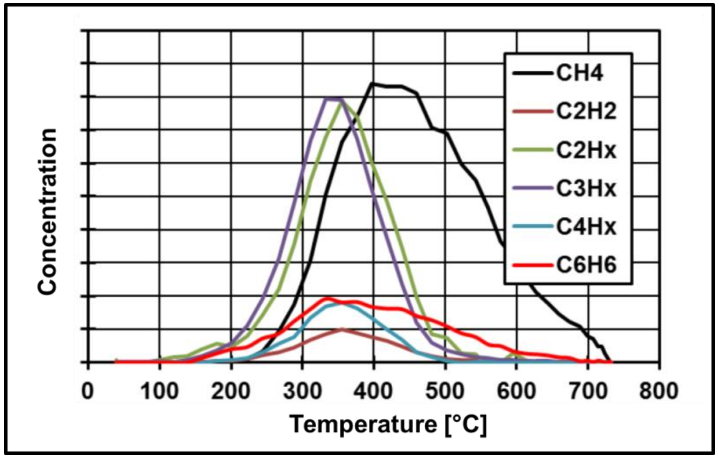
«Natural Raw Materials» (Limestone, Marl, Shale, …)

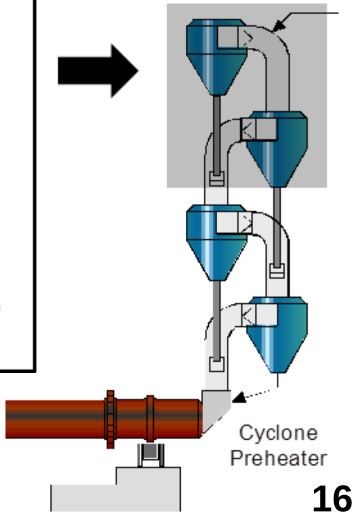
1a

- During heat-up, raw materials expels in the temperature range between 200 and approximately 600 [°C] volatile organic compounds (VOC) *); **it is not an incomplete combustion, it is an EXPULSION** of organic compounds from the raw meal

- «Normal Case»:
  The concentration of the emitted VOC/TOC from raw materials can vary in a greater range, normally between «negligible» and 80 [mgC/m^3]

Compound	**Range of Compounds**
Methane	20 – 40 [%]
C_2-Compounds	25 – 35 [%]
C_3-Compounds	20 – 30 [%]
C_4-Compounds	< 6 [%]
Benzene	“low” to 8 [%]
BETX	“low” to 12 [%]





*) or TOC (Total Organic Carbon)
Similar expression, no difference

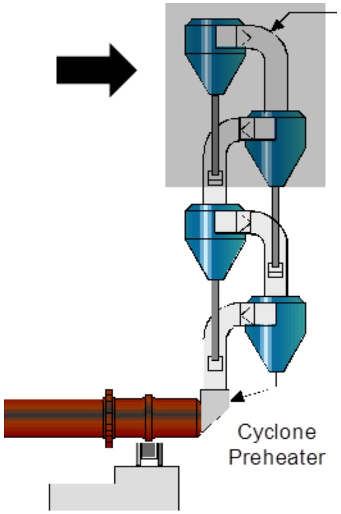
Expulsion from «Natural Raw Materials»

«Natural Raw Materials» continued
(Limestone, Marl, Shale, …)

- «Exceptional Case»:
  The concentration of the emitted VOC exceeds approximately 80 [mgC/m^3]

1a

- Michigan Case (USA)
  (Plant stopped some years ago)
  - From the limestone layers, a black oily liquid flows out.
  - Organic emission of the order of about 4,000 to 6,000 [mg/m^3] (Results from Expulsion Test and emission measurements).
  - Various alkanes, alkynes and alkenes of up to eight carbon atoms could be identified. BETX was present in a rather small proportion of about 2 to 3 [%].
  - Of the cyclic aromatic hydrocarbons, naphthalene, anthracene and phenanthrene were clearly identified, but certainly also other compounds of this type were present.



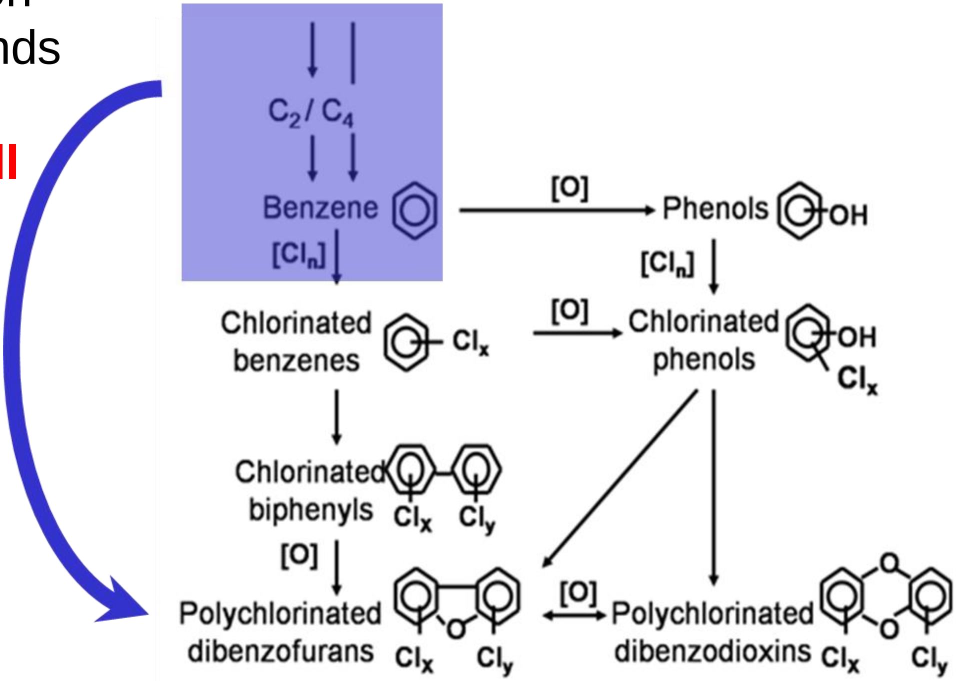
«Natural Raw Materials» and Dioxins

- In general, natural raw material components have no dioxins or furans. However, it is reported that dioxins were found in certain German clays

  According to the working hypothesis of the geoscientists, hot lava and gases could have been the poisonous kitchen of nature some thirty million years ago. … The fingerprint does not fit with today's combustion processes that produce dioxins and the chemically related furans.

1a

- In general the it is a long reaction path from the expelled compounds to dioxins
  Therefore, **there is a very small or even a negligible risk that dioxins can form from «natural raw materials».**



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«Alternative Raw Materials»

1b

Road sweepings and road-holding sludge’s

Fly Ash

Carbide lime (hydrated lime) Körschiztal

Oil contaminated soil

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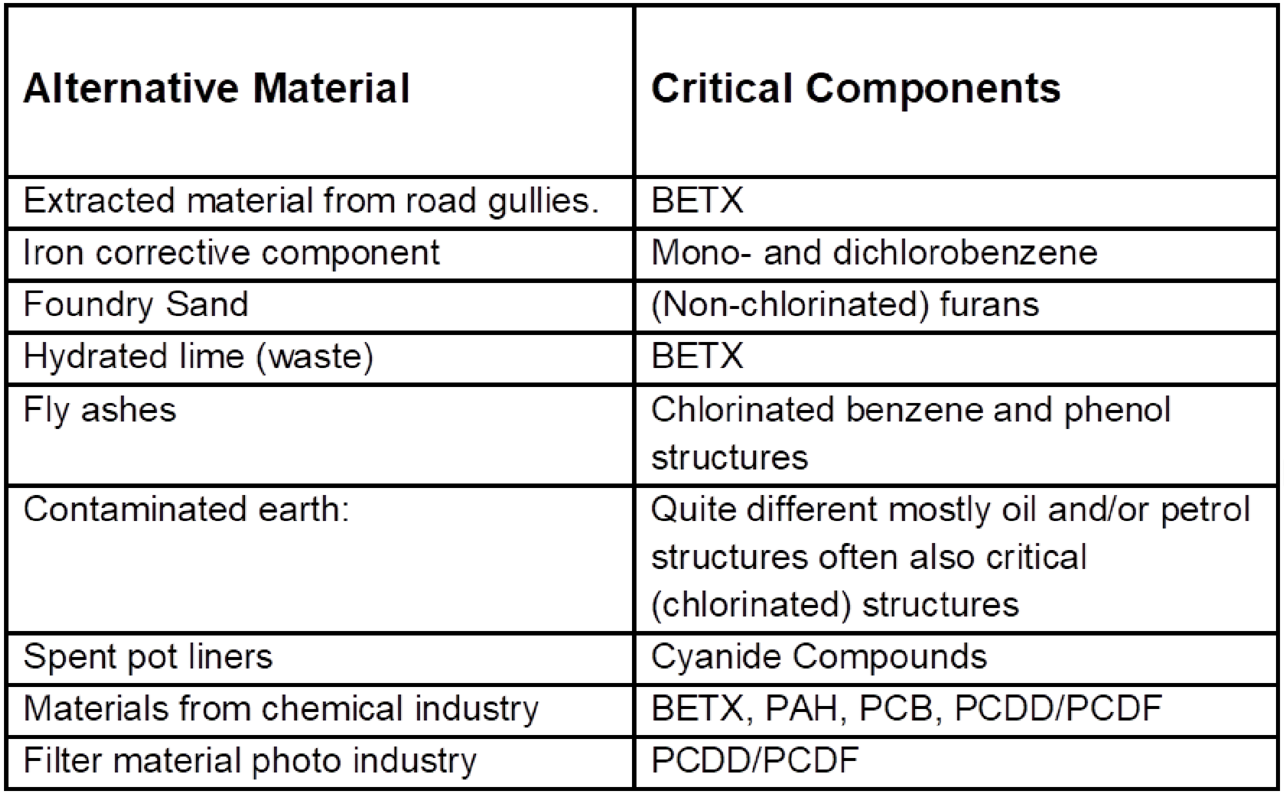
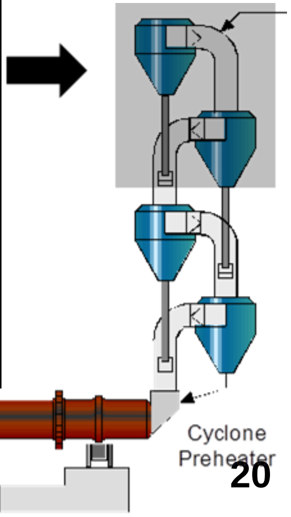
Expulsion from «Alternative Raw Material»

- In alternative raw material compounds it is possible that critical substance, precursors, even dioxins can be present.
- In investigations chlorinated benzenes, phenols, biphenyls and even dioxins were detected.

1b



Alternative Material	Critical Components
Extracted material from road gullies.	BETX
Iron corrective component	Mono- and dichlorobenzene
Foundry Sand	(Non-chlorinated) furans
Hydrated lime (waste)	BETX
Fly ashes	Chlorinated benzene and phenol structures
Contaminated earth:	Quite different mostly oil and/or petrol structures often also critical (chlorinated) structures
Spent pot liners	Cyanide Compounds
Materials from chemical industry	BETX, PAH, PCB, PCDD/PCDF
Filter material photo industry	PCDD/PCDF



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Expulsion from «Alternative Raw Material»

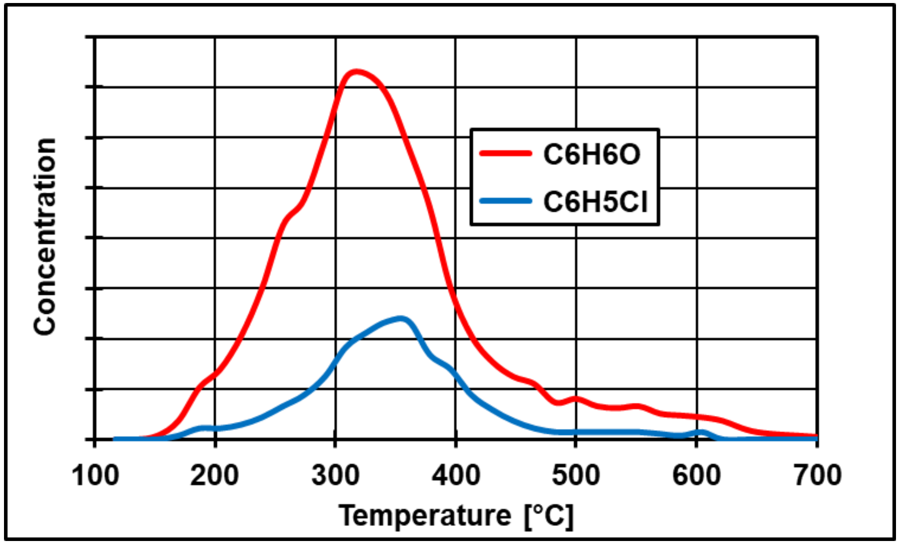
- In such critical «components», the organic compounds are usually only adsorbed. That means the organic substances are only slightly embedded in the base material. Absorption usually does not take place.

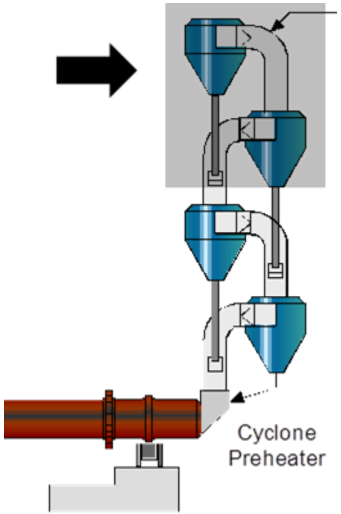
1b

- **Upon heating up such alternative components, the organic components typically evaporate at temperatures below about 400 [°C]**

- Expulsion Test (Labor Test): Expulsion of Phenol (C_6H_6O) and Monochlorobenzene (C_6H_5Cl) from an waste sludge in a cement plant

EXPULSION NOT DEGREGATION





Example #1
Emission of HCB – The Körtschitztal Case

1b

- In an old landfill in the Körschitztal/Austria carbide lime from former times of the carbide production was stored.
- This material consisted of hydrated lime, which could be used well in the cement process
- But the material was contaminated by **hexachlorobenzene (HCB)**.
- Experts from the supplier advised on using the material in the cement plant. They argued that **the material would be oxidized at 800 [°C] and therefore no danger.**
- The material was subsequently added **via the raw material** to the cement kiln system.
- The result was an emission of hexachlorobenzene at the cement works' chimney and associated contamination of the environment.

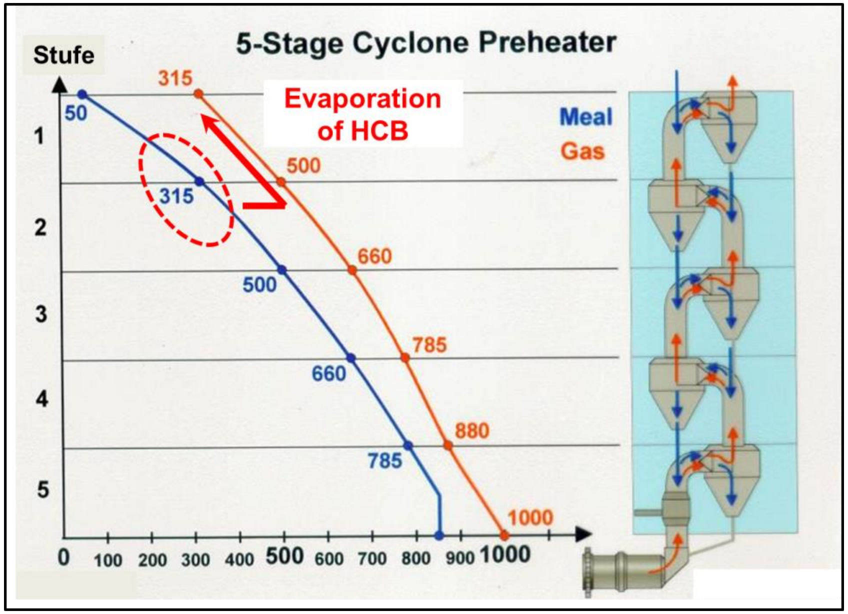
HCB was found in the blood of inhabitants and animals, in the food, in the milk and in the soil.

Example #1
Emission of HCB – The Körtschitztal Case

- HCB vaporizes at 323 to 326 [°C] and never reaches the temperature of 800 [°C] (Destruction temperature) in the cement process
- Consequences:
  The compound HCB is emitted from the heat exchanger, probably builds a circuit between the heat exchanger and filter and is emitted at the chimney.
- **Such material may under no circumstances be added to the raw material.**

1b

- **An Input may only be made via the combustion points of the process**
- The Problem here:
- No specialized knowledge of the cement process
  Remark: Such an input is not an unfortunate isolated case, but occurs too often!



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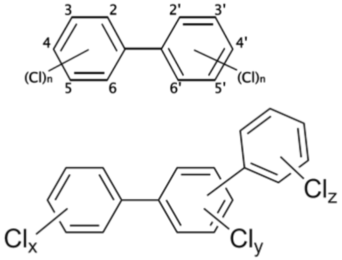
Example #2: PCDD/DF-Formation Sediment Layer from an Oil Tank

- The PCDD/PCDF emission of a 4-stage preheater kiln without calciner was low, in general below 0.01 [ngTEQ/m^3_N] (1013 [mbar], 0 [°C], dry, 10 [%] oxygen).

1b

- As alternative fuel the plant used waste oil on the main burner with the following specifications:
  - Halogens < 1 [%]
  - PCB/PCT < 50 [mg/kg]
  - Water < 7 [%]

  PCB = Polychlorinated Biphenyls
  PCT = Polychlorinated Terphenyls



- The waste oil was stored in a tank and with time a sediment layer at the bottom was formed. Through a misunderstanding, this bottom layer was disposed on the mixed bed (raw material)

Consequence: Formation and Emission of Dioxins

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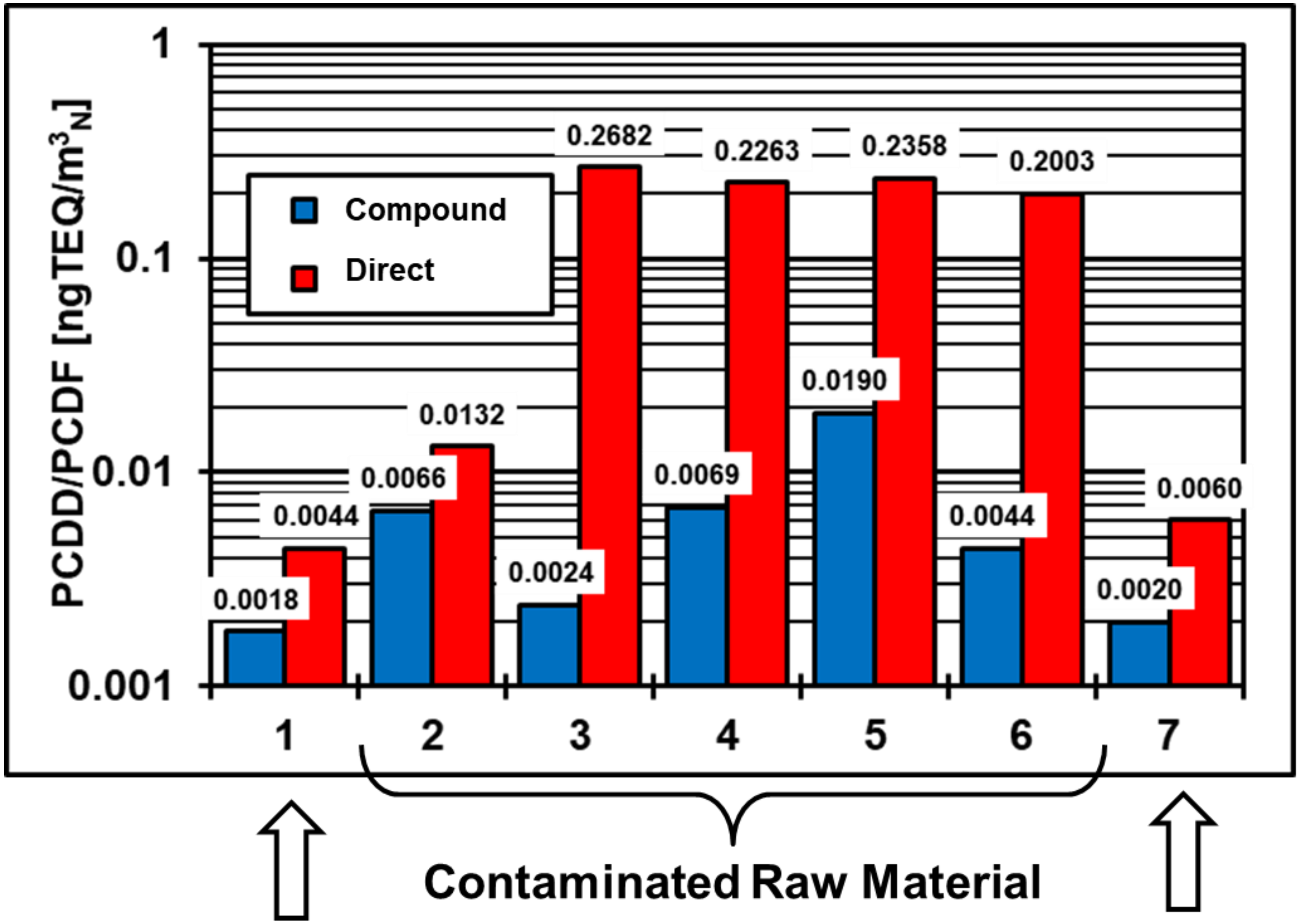
Example #2 – PCDD/DF-Formation
Sediment Layer from an Oil Tank

1b



Contaminated Raw Material

Emissions before

Emissions after

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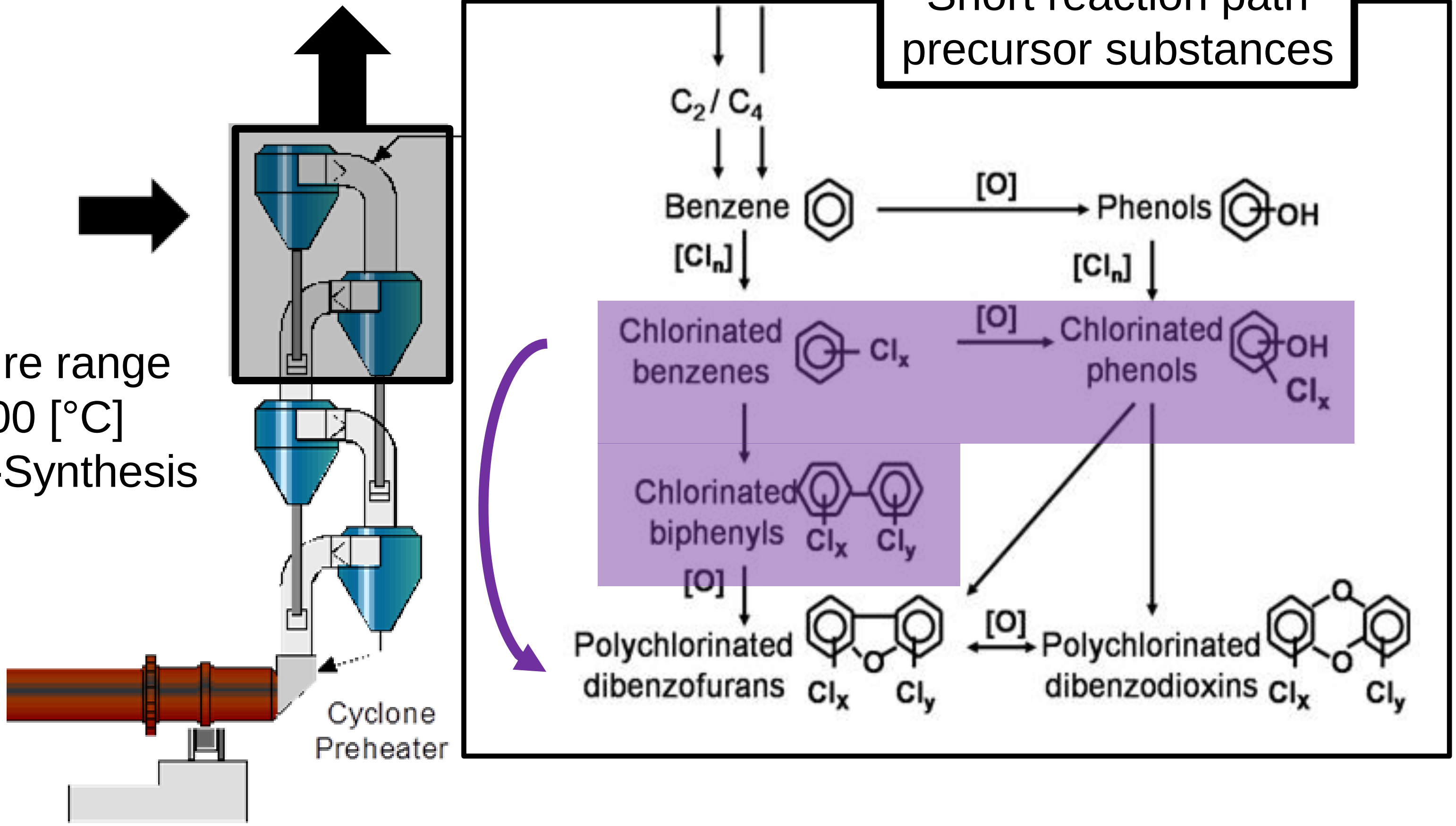
Example #2 – PCDD/DF-Formation
Sediment Layer from an Oil Tank

Evaporation, Recirculation,
Formation of dioxins, ...

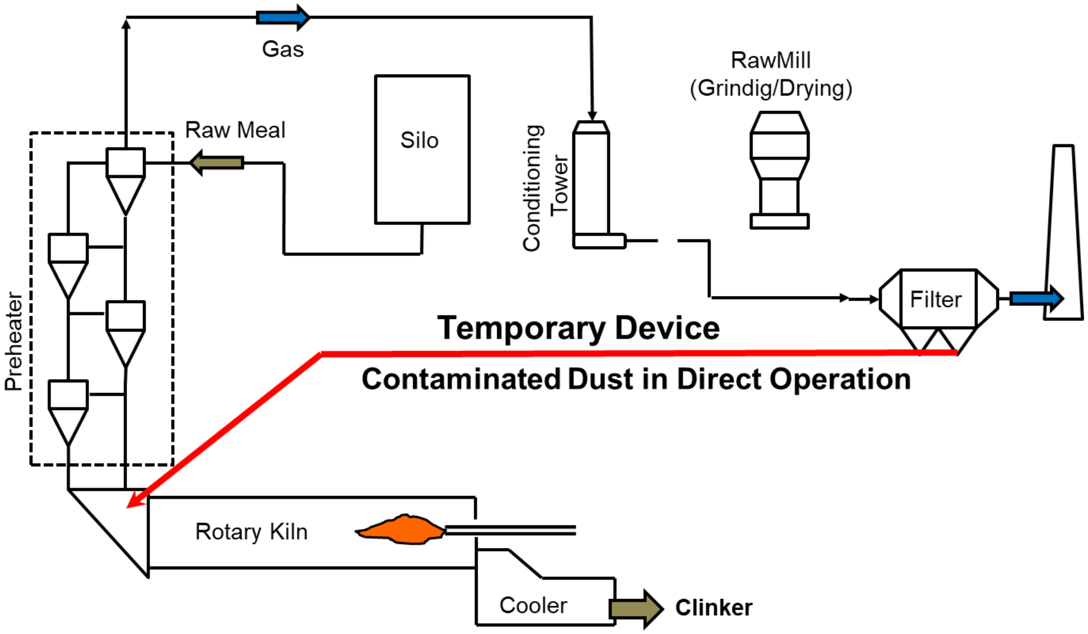
1b

Temperature range
100 – 500 [°C]
«De Novo»-Synthesis


Short reaction path
precursor substances

Example #2 – PCDD/DF-Formation Sediment Layer from an Oil Tank

Immediate Measures



- A rapid reduction of the dioxin content in the dusts was observed
- The originally low emissions were finally achieved again.

- Example shows:
  - Hazardousness of the raw material path
  - Destruction in the right place of the kiln

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Other Dioxin-Cases

- **Fly ash**
  - In two cases, a fly ash and so-called bottom ash was added directly to the raw material, resulting in the formation of dioxins.
  - The ashes were removed from the raw material, eliminating the high dioxin emission problem.
  - It was recommended that these ashes, if they want to use them, not to mix the raw material, but to feed directly to the kiln inlet.
  - The problem is that not all fly ashes are a priori dangerous.

1b

- **Sludge from Ship Canals:**
  - This sludge contained a large amount of PAHs and also PCBs. Dioxins were not found.
  - Blended into raw material, this sludge caused large amounts of dioxins.
  - After removal of this component, the dioxin emission was significantly lower than the limit.
- **Filter Material**
  - In a filter material from the photographic industry PCBs and also dioxins were discovered.
  - The emissions exceeded the limit and the material was removed from the raw mixture

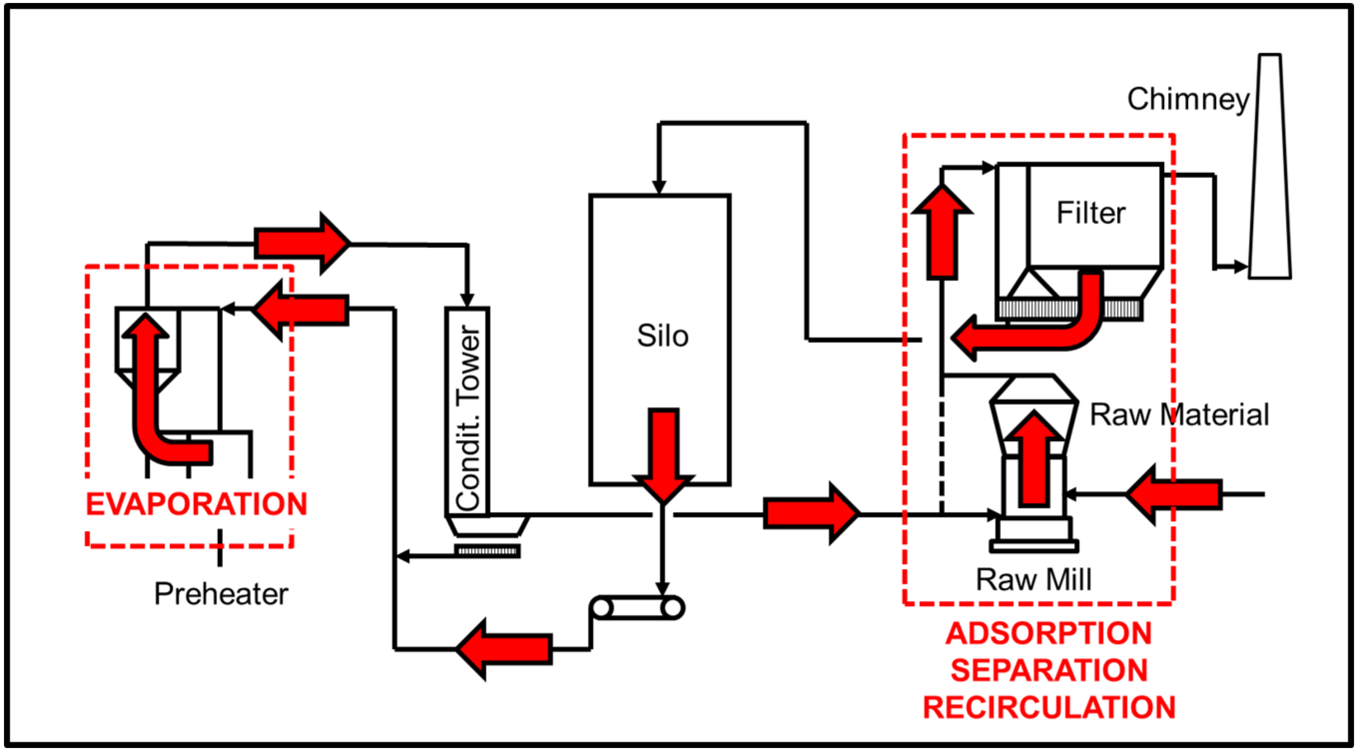
In all cases, the Problem was an Alternative Raw Material Component

The Outer Cycle of Organic Compounds

- Various organic compounds have a cycle (enrichment!) between preheater and filter system
  Proven: Monochlorobenzene, Phenol, Dioxins (PCDD / PCDF)
- Dioxins: Cycle in the critical temperature range between 400/500 (preheater) and < 150/100 [° C] (filter system)
  De-Novo-Synthesis

1b

Cycle



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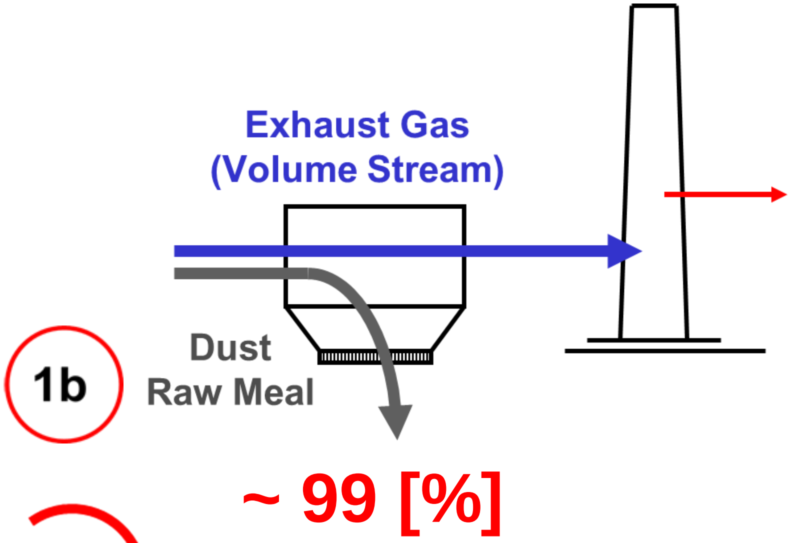
Example #3: PCDD/PCDF Balance on a Filter (EP)



PCDD/PCDF Measurements **~ 1 [%]**

Volume Stream	[m^3/h] *)	150'120	125'740
Raw Meal / Dust	[t/h]	210	8.5
Oxygen	[%]	10.0	7.9
Temperature	[°C]	99.8	148.5

Cycle

Compound operation (running raw mill)

- The compounds are adsorbed in the raw mill on the fresh raw material and the kiln dust
- Temperature is low (99.8 [°C])

→ High adsorption and recirculation via raw meal and dust: ~ 99 [%] of input

→ Low emission: ~ 1 [%] of input

Grindindg/Drying Process
High Mass Flow of Solids
Low Temperature

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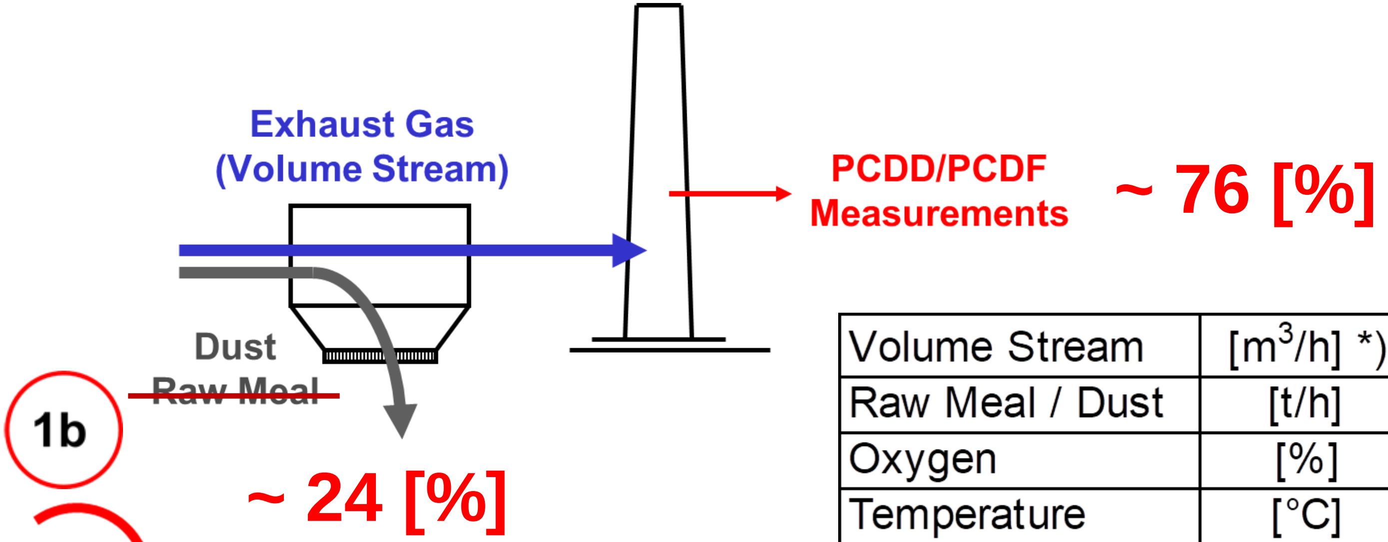
Example #3: PCDD/PCDF Balance on a Filter (EP)



Cycle

Volume Stream	[m^3/h] *)	150'120	125'740
Raw Meal / Dust	[t/h]	210	8.5
Oxygen	[%]	10.0	7.9
Temperature	[°C]	99.8	148.5

Direct operation (stopped mill)

- The compounds are **only** adsorbed on the kiln dust
- Temperature is relatively high (148.5 [°C])

→ Lower adsorption and recirculation
via kiln dust: ~ 24 [%] of input

→ High emission: ~ 76 [%] of input

Grinding/Drying Process
Low Mass Flow of Solids
High Temperature

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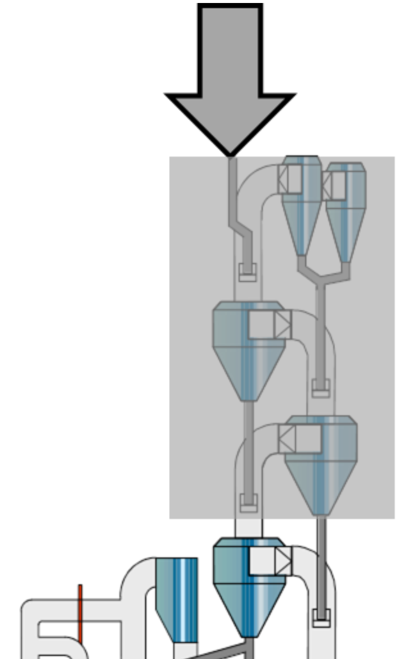
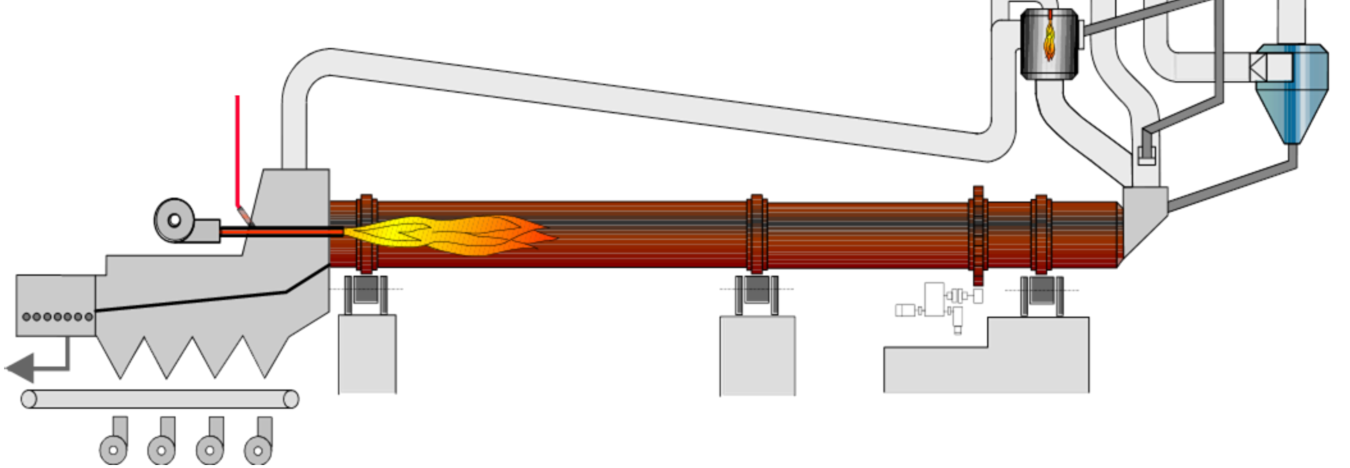
Regulations about the Use of Alternative Raw Materials in Switzerland and in Germany

1b





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Nonsensical Regulations in Switzerland

Switzerland: Waste may be used as a **raw material** in the production of cement clinker if it does not exceed the following limits (total contents)
Maximum input: 5 [%] of the raw total material feed

1b

Compound		**Limit [mg/kg] (dry substance)**
Polychlorinated Biphenyls	PCB 1)	10
Benzene	C_6H_6	1
Polyaromatic Hydrocarbons	PAH 2)	350
Benzo(a)pyrene	$C_{20}H_{12}$ 3)	3 (10)

Dangerous Nonsense

1) Sum of 6 congeners x 4.3 (IUPAC no. 28, 52, 101, 153, 180)
2) Sum of 16 PAH (EPA list)
3) Plan: increase to 10 [mg/kg]

1.) These components evaporate from the raw material and are (partly) emitted at the stack
2.) This has been proven scientifically by experiments und tests in various plants

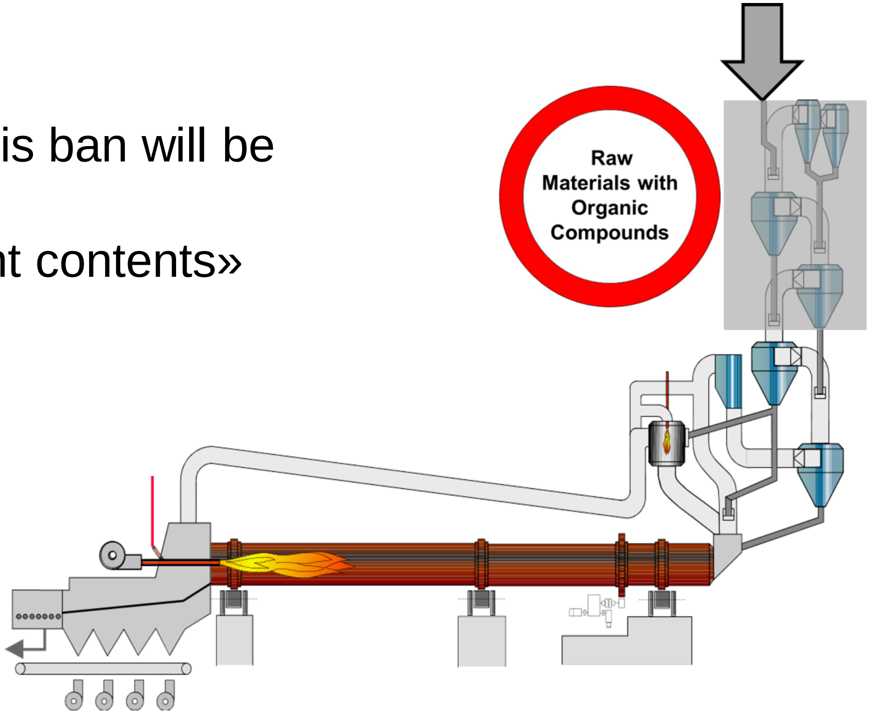
Regulations in Germany

1b

The German regulations (TA Luft 2002 and draft 2008) takes into account the possibility of the emission of organic substances by contaminated raw materials. In Section 5.4.2,3 it is stated:

"ORGANIC SUBSTANCES - ... As far as waste with relevant contents of organic ingredients as raw materials (Remark: wastes, which are added to the raw material) *are used ... ..., an addition should be made via the kiln inlet or the calciner".*

There are legitimate doubts that this ban will be respected throughout Germany.
Problem: Interpretation of «relevant contents»



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Raw Material - Conclusions

1a

1. **«Natural raw materials» are mostly not problem**
(High emissions of aliphatic compounds and BETX can occur. High emissions of PCB and PCDD/PCDF can be excluded)

2. **Alternative raw materials can contain critical organic or chloro-organic substances and should not be added to the raw material / raw meal!**
(Not even if government regulations permit)

RULE

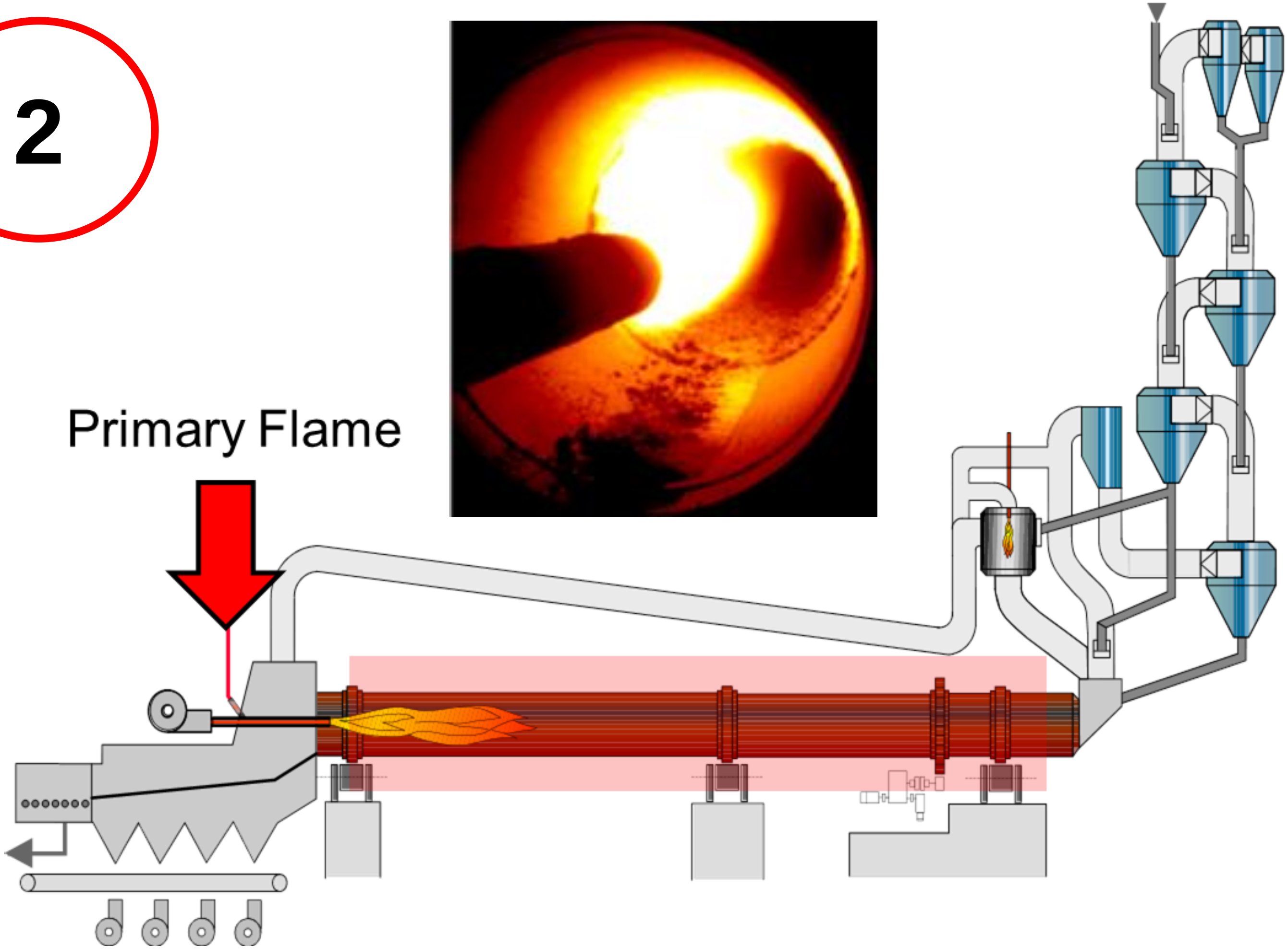
1b

3. **Organic components in alternative raw material may also be precursors of dioxins**
(The dioxin formation from such substances is proved)

4. **Alternative raw materials must be checked with adequate analysis methods.**

V. The Influence of the Primary Flame

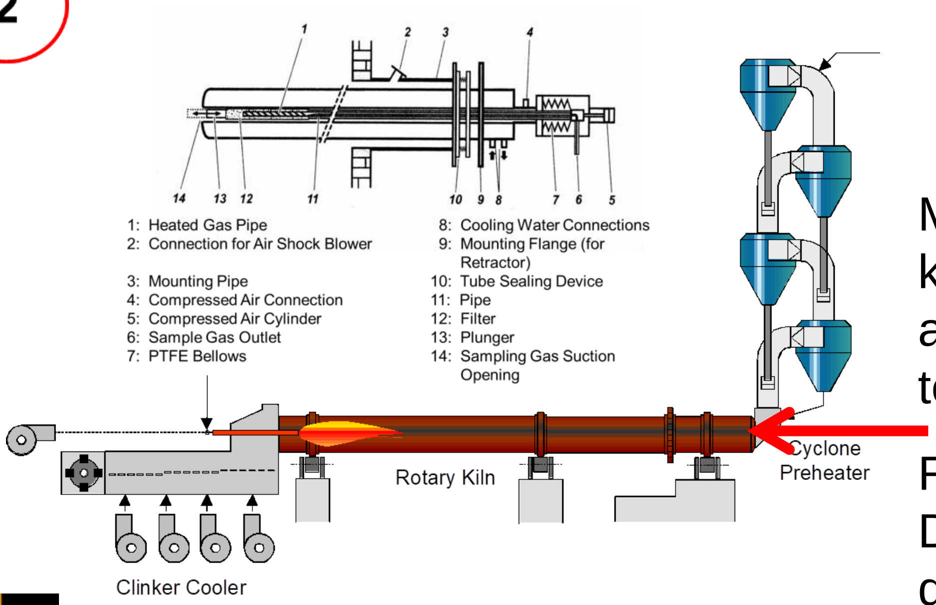
2



Oxidation in the Main Flame

- The maximum temperature in the flame is around 2000 [°C]
- Gas temperature in the rotary kiln section is at least 6 to 8 [sec] above 1100 [°C]
- Because of the clinker quality the burning process in the area of the sintering zone must be operated with excess air

②



Measurement on a 4-stage preheater kiln via a special kiln inlet probe with a flame ionization detector and temporarily with a mass spectrometer.

Results:
During 8 weeks no organic compound detected
(below detection limit)

Primary Flame - Conclusions

1. **PAHs, chlorinated benzenes, PCBs and also PCDD / PCDF, or their precursors are completely oxidized.**
   A formation of such substances in the rotary kiln part of the kiln system can be completely excluded.

②

2. **No influence if conventional (coal, oil, …) or alternative fuels are used**

RULE

3. **Hazardous wastes with a content of more than 1 [%] of halogenated organic substances must be added to the main flame.**

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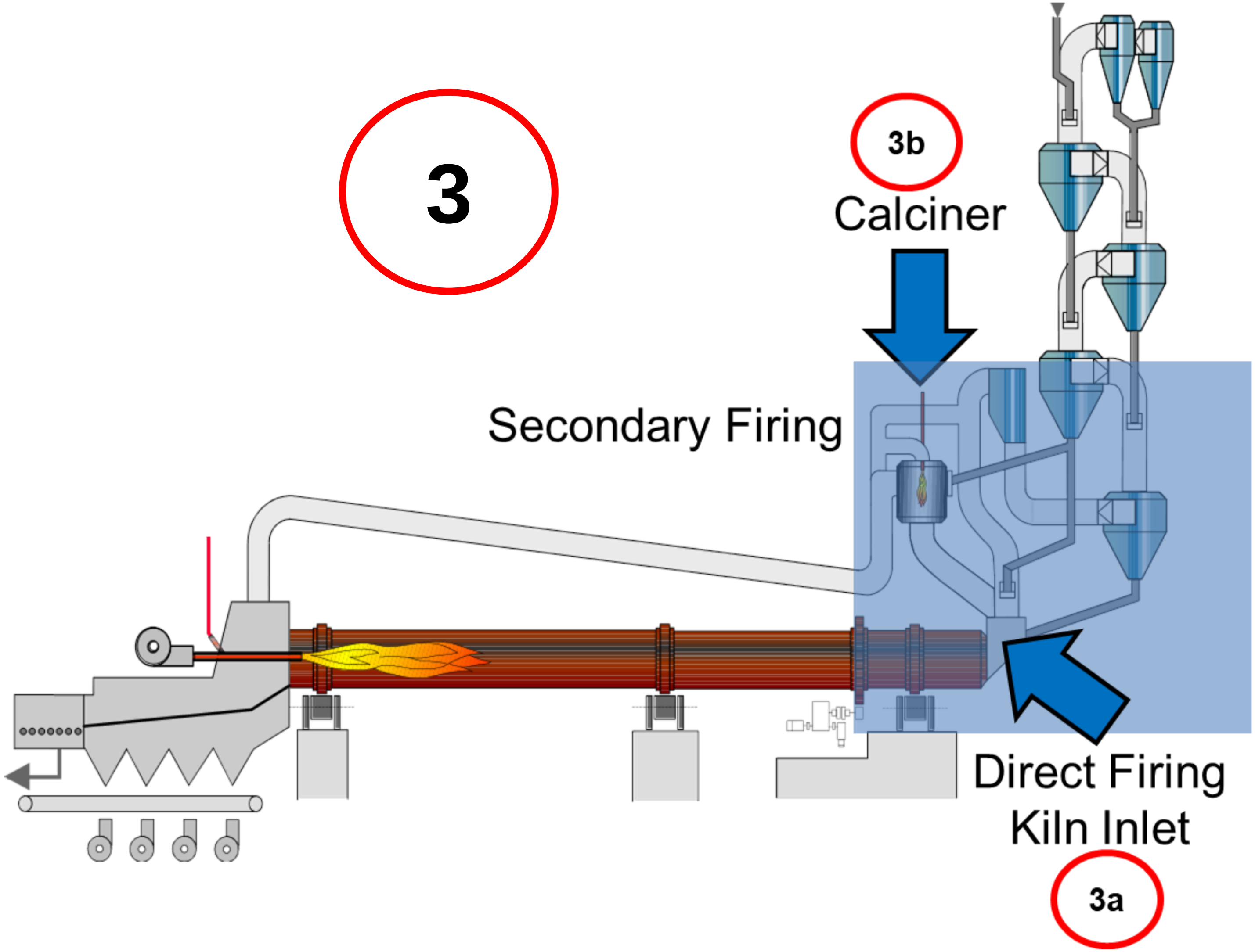
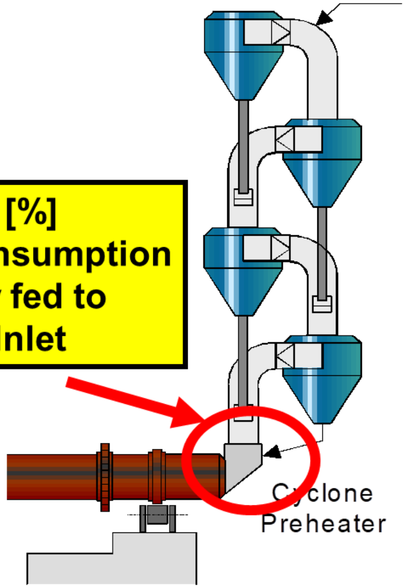
VI. Secondary Firing



Direct vs. Calciner Firing



< 20 [%]
of Heat Consumption
directly fed to
Kiln Inlet

3a

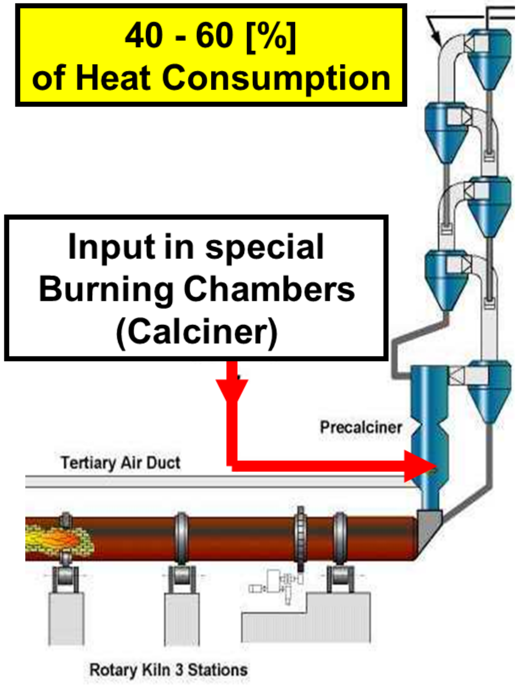
Mostly used for fuels which are in large pieces, e.g. used tires.

Local reducing conditions can reduce NOx

Dwell time often too short

40 - 60 [%]
of Heat Consumption

Input in special
Burning Chambers
(Calciner)



3b

Temperature between 850 (exit) and 1100 [°C] (inlet)

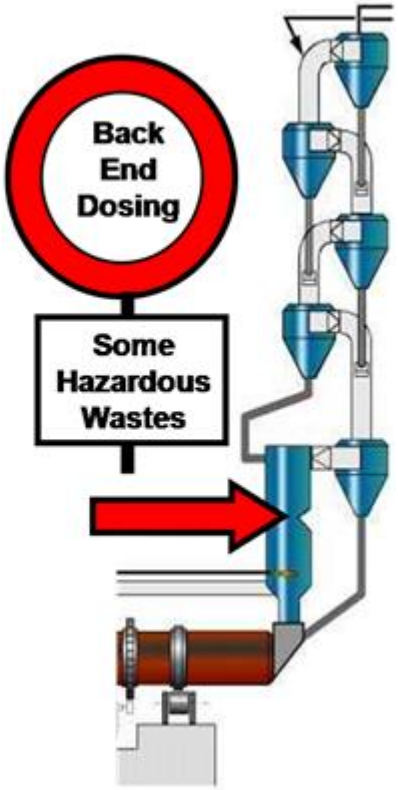
Dwell time depends on volume of calciner

Mostly staged combustion (multiple fuel input points) -> reduction of NOx ($2\ NO + CO \rightarrow N_2 + CO_2$)

Rule about Secondary Firing Restriction in Europe

3a

3b



- Co-incineration plants shall be designed, equipped, built and operated in such a way that the gas resulting from the co-incineration of waste is raised in a controlled and homogeneous fashion and even under the most unfavorable conditions, to a temperature of 850 [°C] for two seconds.

  Direct firing at the kiln inlet can in general not meet this requirement (often not checked and therefore accepted)

  If **hazardous wastes** with a content of more than 1 [%] of halogenated organic substances, expressed as chlorine, are co-incinerated, the temperature has to be raised to 1’100 [°C].

  This requirement can not be met in calciners in the rule.

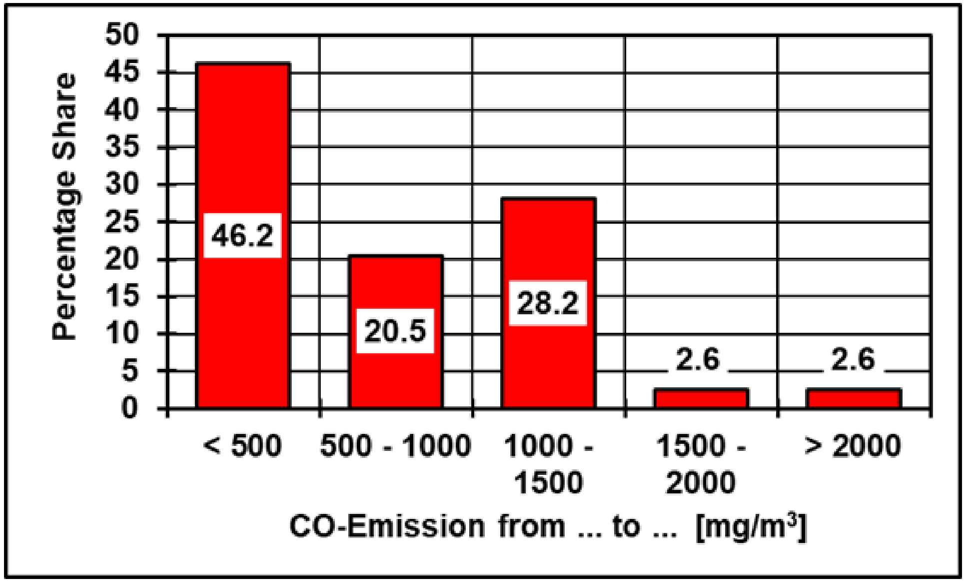
Reducing Combustion in Secondary Firings

- Investigations have shown that little carbon monoxide develops from the raw materials. The maximum from raw materials is about 500 [mg/m^3], mostly .
- The evaluation of the annual averages of carbon monoxide emissions in Germany in 2017 shows that some cement plants sometimes even significantly exceed this value.

3a

3b

- **Part of this pollutant emission must therefore come from the secondary combustion.**



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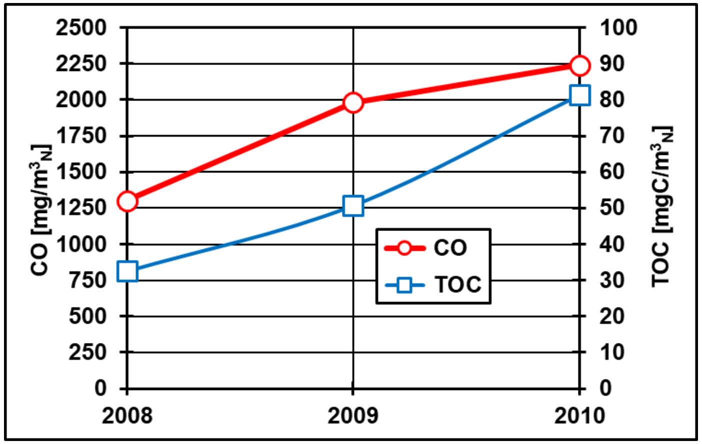
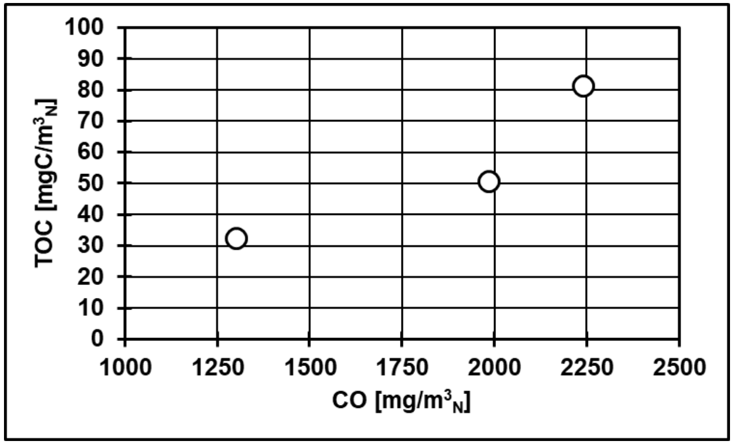
Reducing Combustion in Secondary Firings

- The daily averages of all German cement plants from 2008 to 2010 were evaluated.
- In individual plants both the yearly average CO emissions and also the TOC emissions increased significantly.
- Example of an individual plant with tires combustion.

3a

3b





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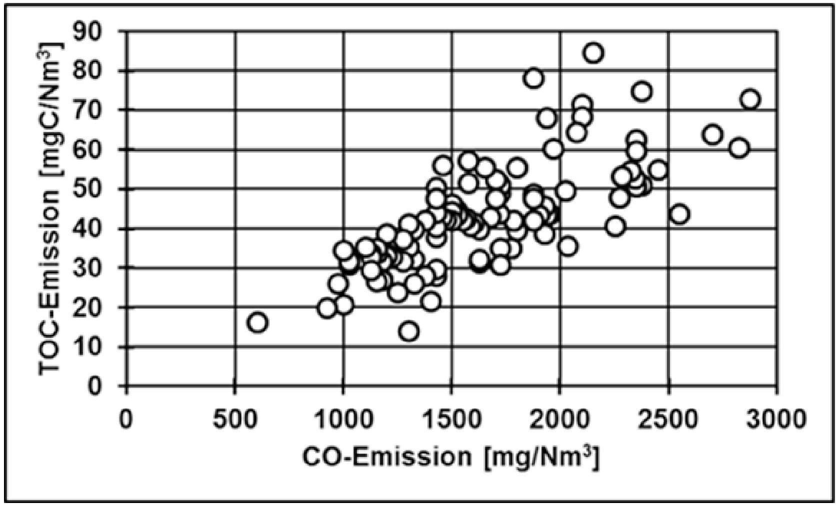
Reducing Combustion in Secondary Firings

- Such behavior can not be produced by the alternative raw materials.
- The reason lies in the combustion, more precisely in the secondary combustion.
  - Reducing conditions (Partly or global)
  - Too high input of fuel, too little air, air distribution not optimal, …

3a

3b

Important: Correlation between CO and TOC



Limits in this State of Germany Exemption???

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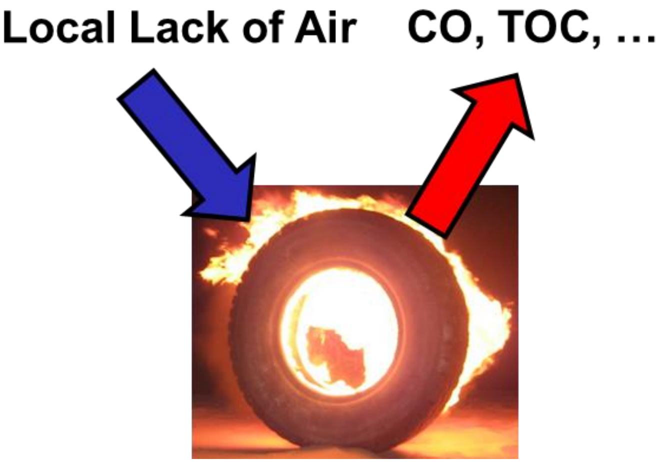
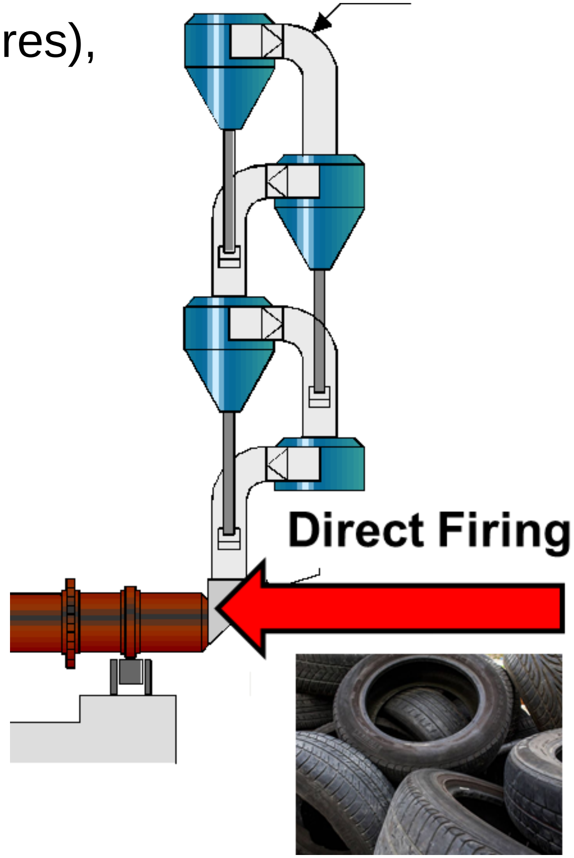
Direct Firing

- In the direct fuel input into the kiln inlet, in particular in the supply of bulky or lumpy fuels (example: tires), it comes locally to reducing conditions and the formation of carbon monoxide (CO) and organic compounds (TOC).

3a



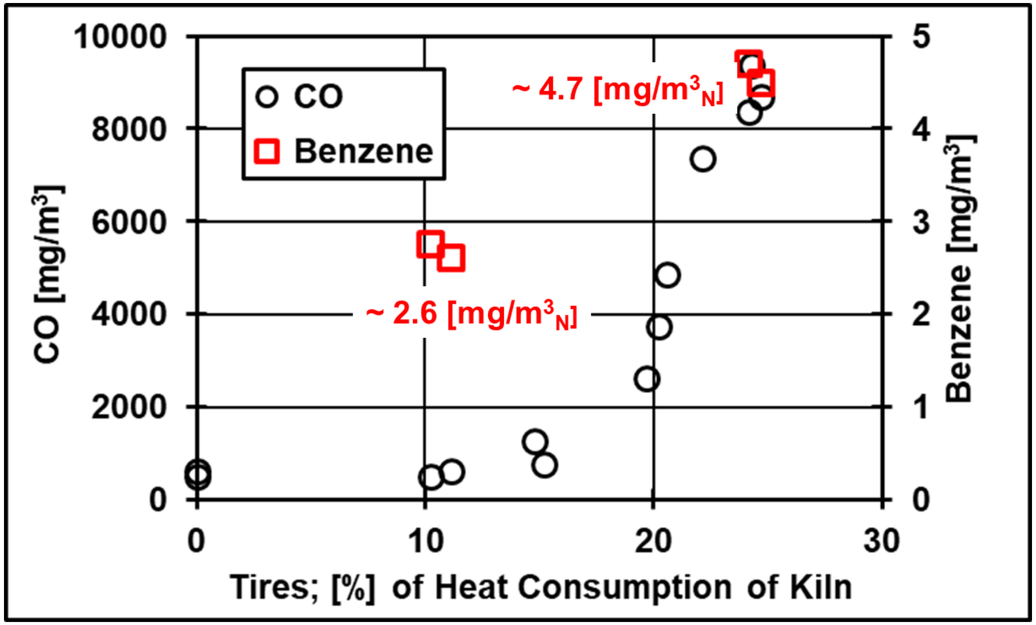


- These compounds can be degraded in the area of the kiln inlet partly insufficient and there is an additional emission from the secondary firing.

Example #1: Tires and CO-Formation

- 4-stage preheater ; production 3000 [t/day] with tire input at kiln inlet
- Test: The input was increased from zero (no tires) to about 25 [%] of the required heat consumption.
  - Below about 15 [%] of the heat consumption, the carbon monoxide emission at the chimney remained more or less constant at about 500 [mg/m^3].
  - Over 15 [%] of the heat consumption, the CO emission drastically increased because the locally formed CO could no longer be completely oxidized.
  - Benzene was also measured with activated charcoal tubes during the tests. It turned out that this pollutant also increased significantly.

3a

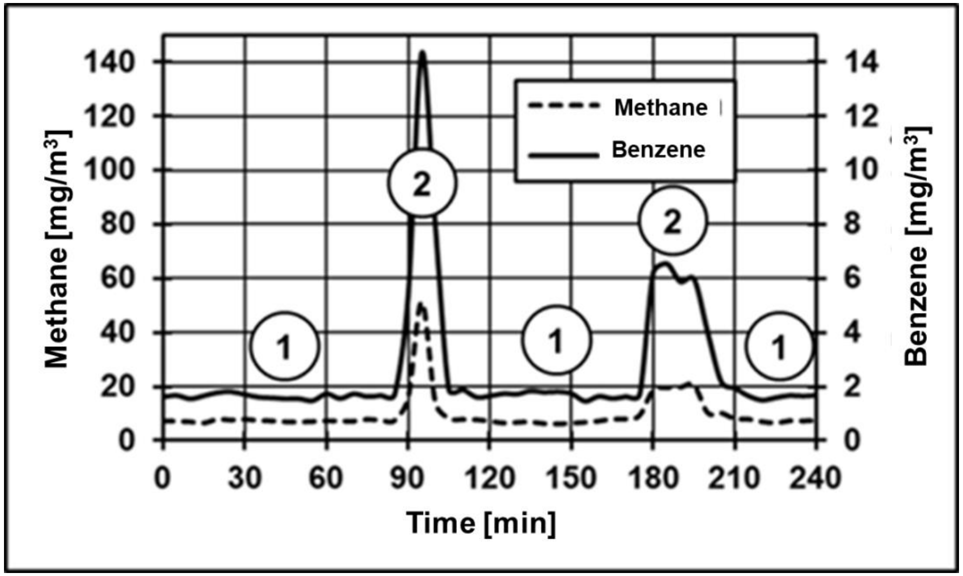


Example #2: «Overfeeding Test»

- In another cement plant, during short periods additional tires were fed into the kiln via the double flap system.
- Phases 1: About 10 [%] tires (based on the total heat consumption) were burned. The emissions of TOC (total organic carbon), methane, benzene and other aliphatic compounds remained more or less constant. The level and the composition of the emissions roughly correspond to the emissions from the raw materials.

3a

- «Overfeeding»-Phases 2: The emissions of methane and benzene increased quite markedly, while the aliphatic compounds (C_2-, C_3-compounds) increased only insignificantly.



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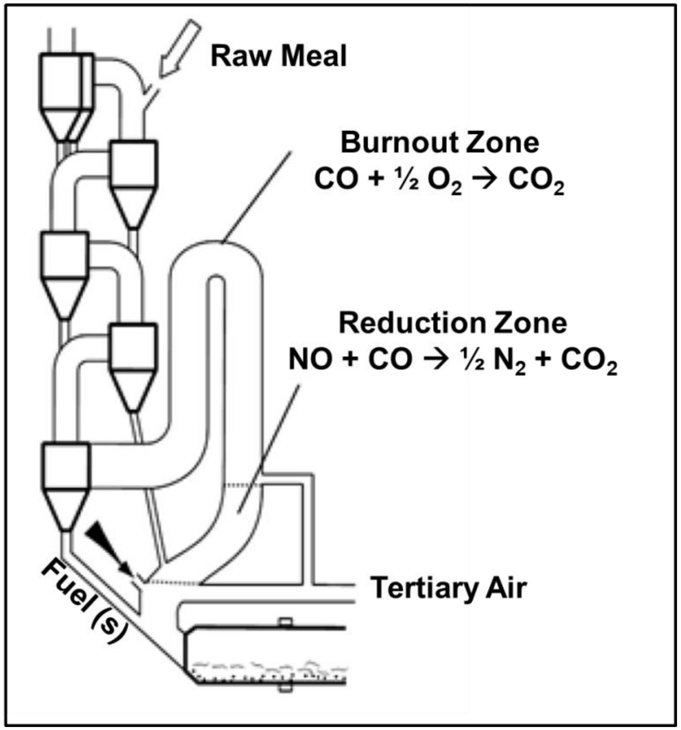
Calciner Firing

3b

- In calciners the so-called technique of staged combustion is 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, the right fuel distribution and amount, etc. This is not the case in many calciner, and as consequence carbon monoxide (CO) and other organic compounds are emitted from the calciner firing.



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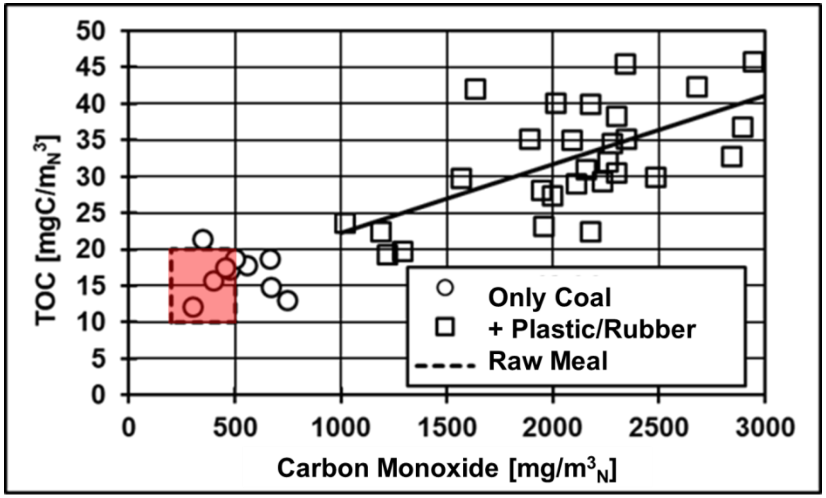
Example #3: Input of Alternative Fuel in a Calciner

3b

- In a cement plant about 50 [%] of the heat consumption was generated in the calciner with coal (w/o AF).
- From the raw material analysis (Expulsion Test), the following emissions were predicted (red square):
  - CO: 350 ± 150 [mg/m^3]
  - TOC: 15 ± 5 [mgC/m^3]
- When operating with coal, the illustrated emissions (circles) were measured (daily averages).
- Part of the coal, about 30% was replaced by plastic and rubber chips Emissions increased significantly (squares). One problem was that the supply was not constant and blockages occurred again and again. Furthermore, the calorific value of the mixture fluctuated in greater ranges.



- The feed was improved and a better mix was used later. Unfortunately, there is no data available, but the plant reported that the CO emission could be stabilized at around 1000 to 2000 [mg/m^3] and TOC emissions at around 25 [mgC/m^3].

Experiences with Secondary Firings

1. With higher input, depending on the fuel, there is an increase in carbon monoxide (CO) emission
   This is a measure for the emission of organic emission and should be limited.
2. As a rule, aliphatic and BETX compounds are emitted. Polyaromatic hydrocarbons (PAH) or similar compounds were only emitted at higher CO levels.
3. Certain waste fuels have been found to increase specific aromatic compounds.
   Polystyrene → styrene
   Polyurethane → benzene;
   Tires and rubber → Benzene, methane
4. Chlorinated compounds, e.g. monochlorobenzene, could not be detected. But that does not mean that they could not occur under unfavorable conditions.

3a

3b

Secondary Firing - Conclusions

1. Hazardous waste containing more than 1 [%] of halogenated organic substances expressed as chlorine shall not be incinerated in secondary combustion. Prohibition!

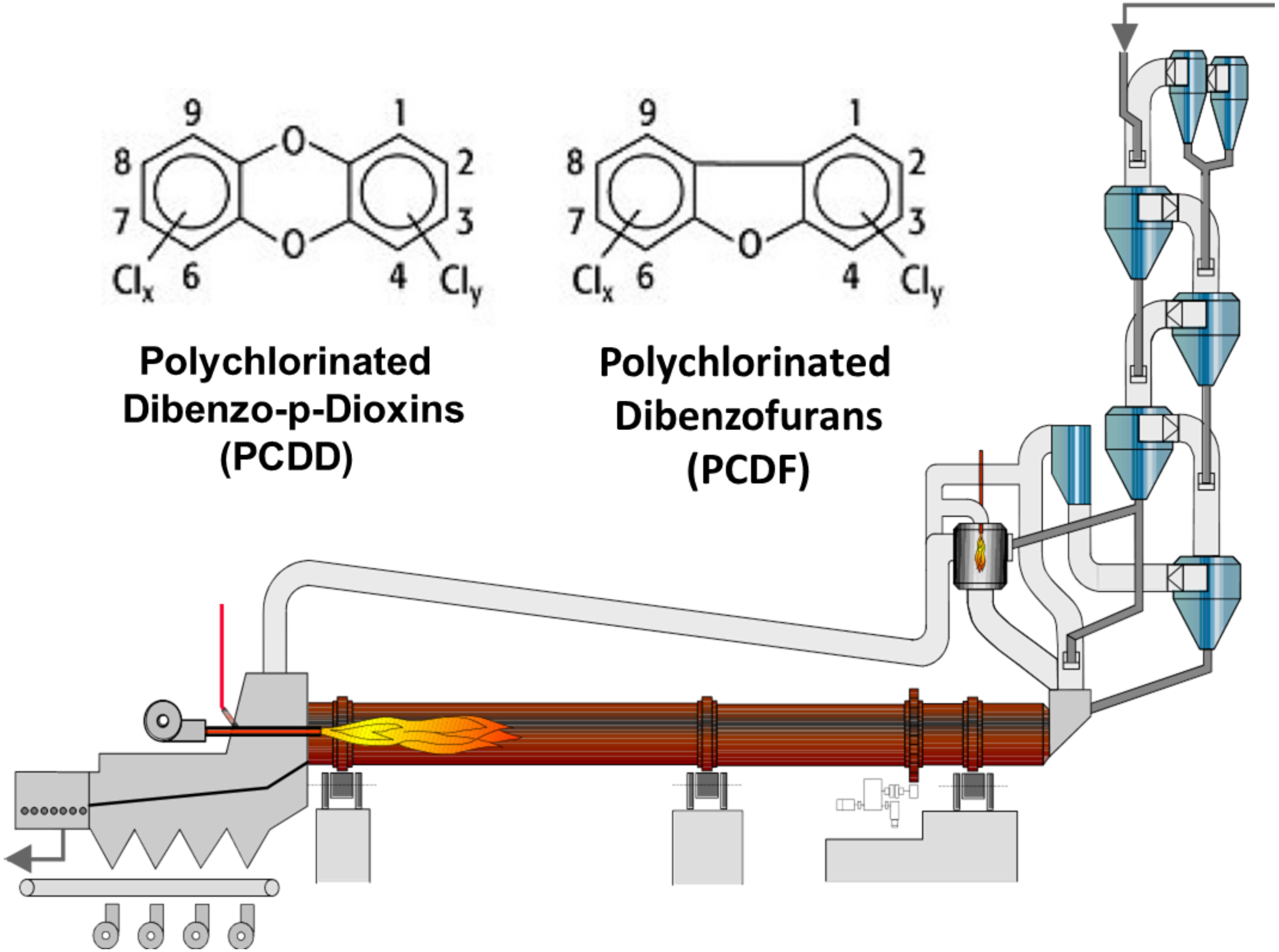
2. Good burnout of the fuel (s), especially of coarse fuels (e.g., tires) is to be ensured. Excessive CO emissions should not be accepted under any circumstances.

3a

3b

3. As a rule, aliphatic and BETX compounds are emitted. Polyaromatic hydrocarbons (PAHs) or similar compounds were more likely to be emitted in traces and especially under reducing conditions.

VII. Dioxin-Formation in Cement Kilns



Polychlorinated Dibenzo-p-Dioxins (PCDD)

Polychlorinated Dibenzofurans (PCDF)

Dioxin-Formation in Cement Kilns

Very important for the formation of dioxins is the element chlorine in the kiln system

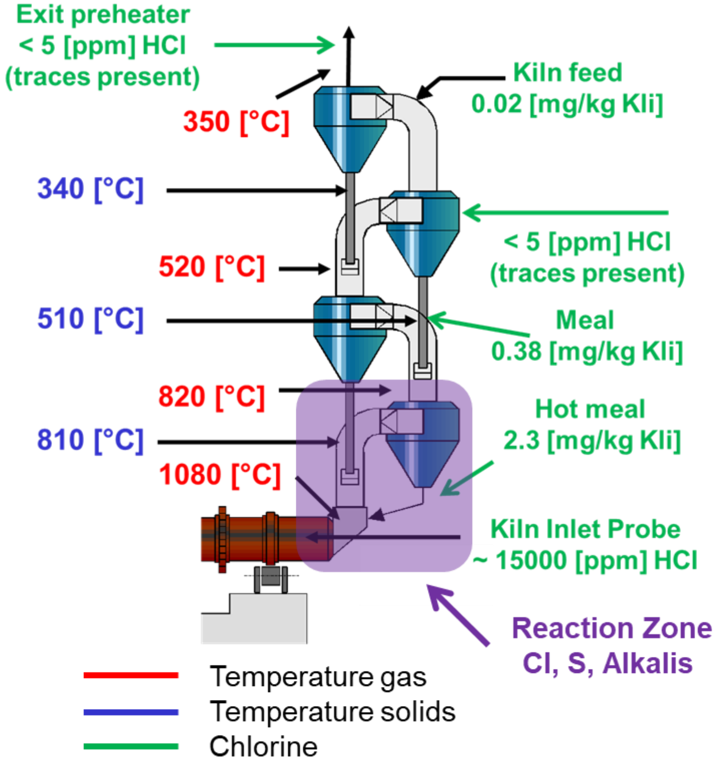
- **Incinerators:**
  - Chlorine is produced by burning plastic, etc., and is eliminated from the exhaust gas at the end of the process.
  - A material to be heated, such as in the cement kiln, is absent and therefore there is no reaction with such material
  - (Gaseous) reactive chlorine compounds are formed at temperatures below 800 [°C]

- **Cement plants:**
  - Chlorine is supplied through the raw material and the fuels.
  - **Chlorine reacts with the raw material above 800 [°C] and forms a cycle between lowest cyclone(s) and rotary part.**
  - (Gaseous) reactive chlorine compounds cannot be formed (or only in traces) at temperatures below 800 [°C]

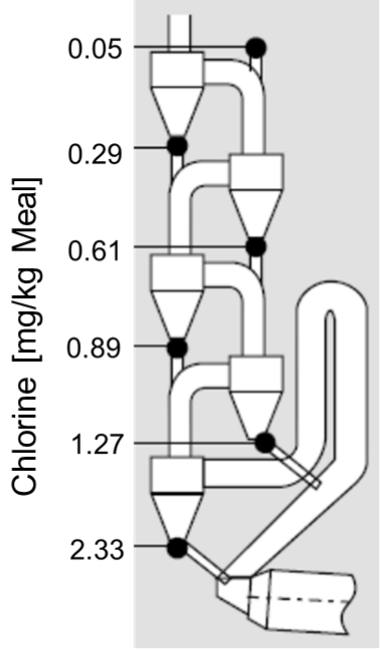
Chlorine in the Preheater

VDZ: During the clinker burning process gaseous inorganic chlorine compounds are either not emitted at all or only in very small quantities. Owing to the alkaline kiln gas atmosphere, the formation of hydrogen chloride (HCl) in the exhaust gas can be largely ruled out.

4-stage preheater
with 15 [%] secondary firing

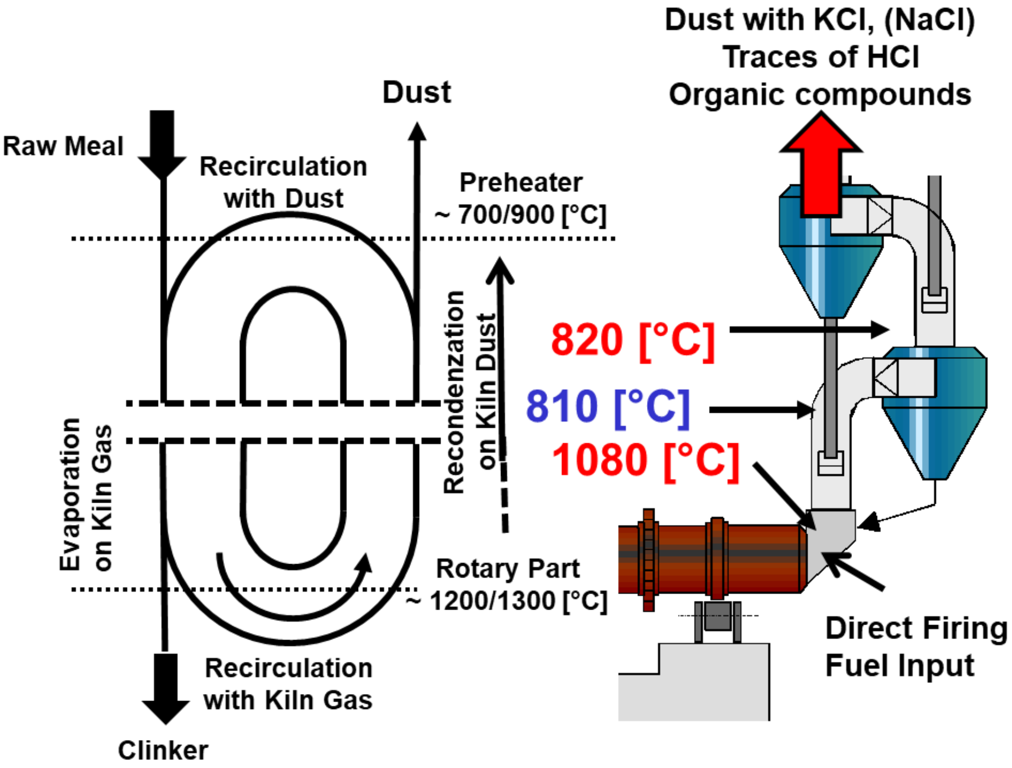


5-stage preheater with calciner
and secondary firing



Measurement VDZ

Dioxins: Chlorine Behavior of Chlorine



Behavior of chlorine in the reaction zone

1. Chlorine **first** combines with the alkalis to form potassium chloride (KCl) and sodium chloride (NaCl).
2. The remaining chlorine, if present, combines with the calcium to form calcium chloride ($CaCl_2$).
3. A reaction with organic compounds (chlorination) in this zone could not be detected

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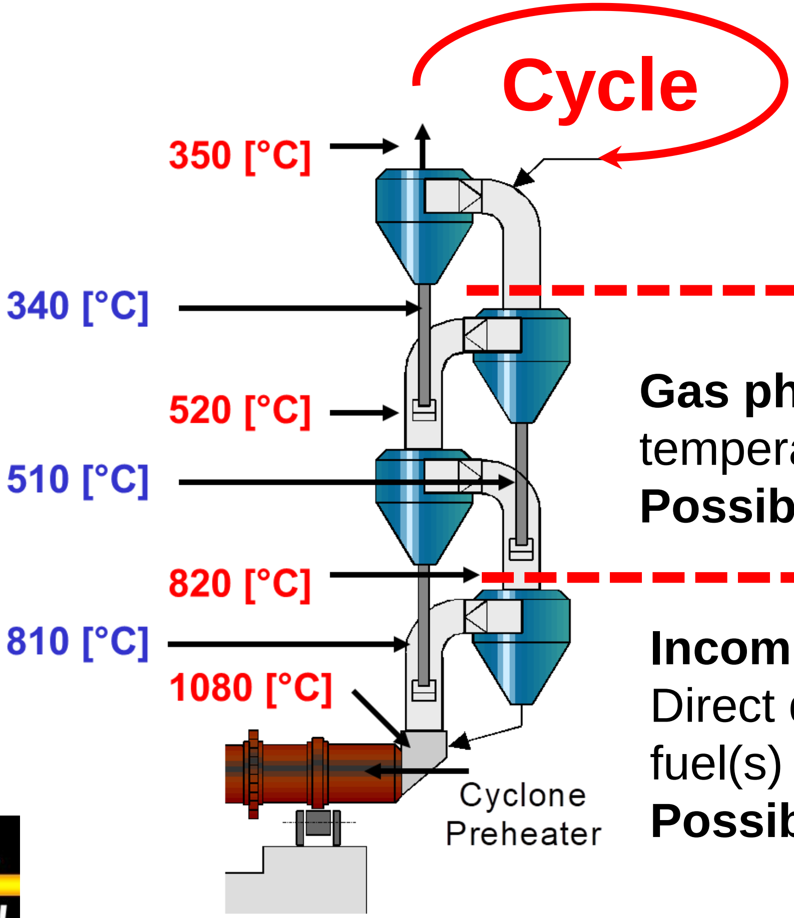
Formation of Dioxins in the Preheater System



«De-Novo-Synthesis»: Heterogeneous reaction of organic compounds and chlorine in the temperature range between 200 to 400 [°C].
Additional influence:
Long residence time of critical compounds in the range 200/400 [° C]

Gas phase reaction of precursors in the temperature range between 400 and 800 [°C]
Possible, rather small

Incomplete Combustion:
Direct development of precursors from the fuel(s)
Possible, rather small

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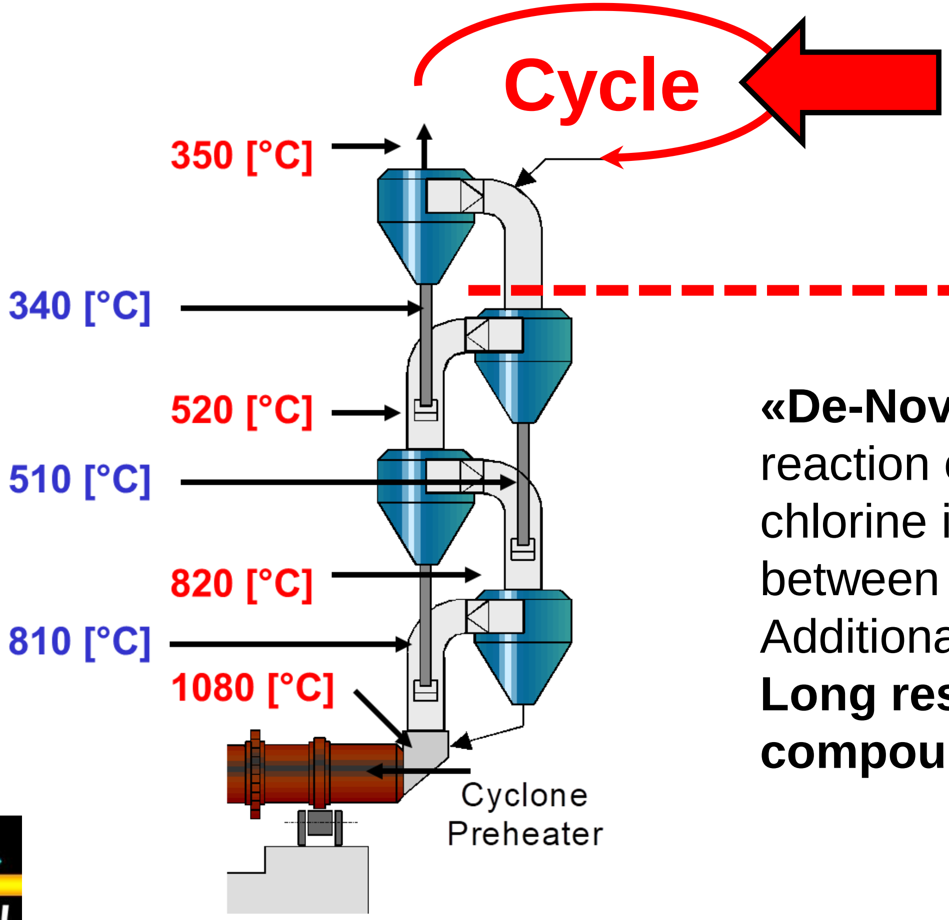
Formation of Dioxins in the Preheater System



Critical Compound in
Raw Materials
Great Risk!

«De-Novo-Synthesis»: Heterogeneous reaction of organic compounds and chlorine in the temperature range between 200 to 400 [°C].
Additional influence:
Long residence time of critical compounds in the range 200/400 [° C]

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Conclusion Dioxins

1. **Alternative material components must not contain critical organic compounds!**

2. **In the field of secondary firing (direct firing or calciner), precursors are formed when zones with strongly reducing conditions are present.**

3. **Chlorination of organic compounds in the upper part of the heat exchanger is possible but rather weak, since only little chlorine is present and additionally in the form of chlorides. Metals, which could act catalytically, are only present in traces.**

RULE

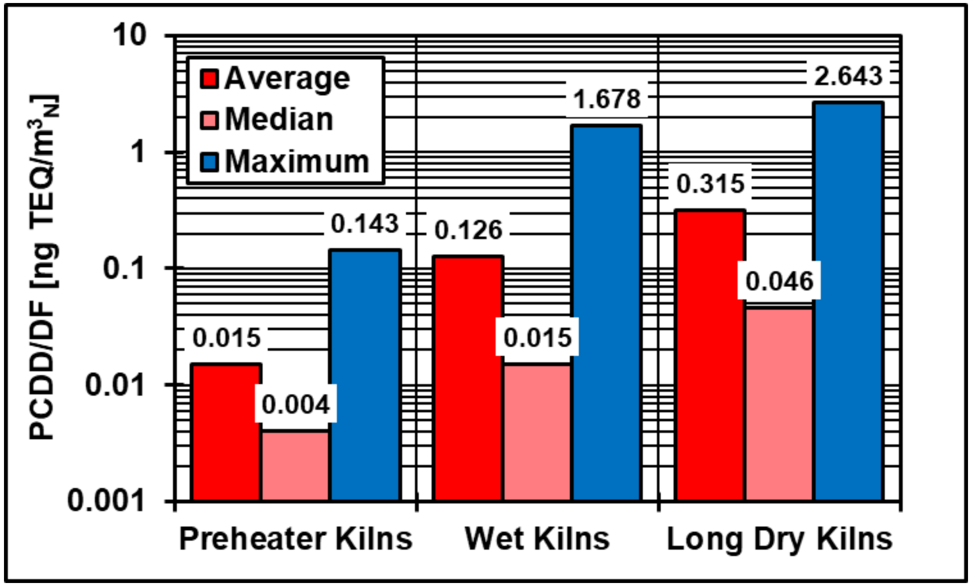
4. **Prevent reducing conditions and guarantee a good burnout of the fuel(s), especially of coarse fuels, e.g. tires Check the CO-emission!**

VIII. PCDD/PCDF in Different Kiln Systems

- **All statements about dioxins are only correct for modern kiln with preheaters not for older kilns. They work differently!**
- 2002 the PCDD/PCDF measurements of a cement group and results of official measurements were collected. Today, such statistics are no longer possible because most wet and long dry kilns have disappeared.

	SP Kiln	**Wet Kiln**	**Long Dry Kiln**
Number	40	28	16
Average	0.015	0.126	0.315
Median	0.004	0.015	0.046
Maximum	0.143	1.678	2.643

SP Kiln = Suspension Preheater Kiln



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I hope you're not smoking your head now.

Thank you for your attention!