

Minimizing Dioxin and Furan Emissions during Zinc Dust Recycle by the Waelz Process

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The Waelz process is a classic method for treating steel plant dusts containing zinc and lead. This process makes especially exacting demands on the off-gas cleaning system because, in most cases, the feed material is heavily contaminated with organic and inorganic components. As a result of the thermal treatment of the residues, dioxins and furans are liberated on the raw-gas side, requiring the installation of additional off-gas cleaning systems. Using as examples two Waelz kiln plants, this article describes the primary measures that minimize the formation of dioxins and furans.

INTRODUCTION

As zinc consumption in the steel industry increases, the recycling of zinc-containing residues is gaining in importance. The Waelz process is among the methods with the largest treatment capacity for reprocessing such secondary feed materials.¹

Exacting demands are made on the off-gas cleaning system for Waelz plants. During the thermal treatment of the residues containing diverse organic and inorganic pollutants, dioxins and furans are set free and/or forming on the raw gas side that require highly effective cleaning units to curb emissions.

Issues related to polychloridibenzodioxines and dibenzofurans (PCDD/F) have been investigated in Europe since 1976. The need to reduce PCDD/F emissions poses a serious challenge for secondary metallurgical smelting facilities because the problems inherent in those highly toxic compounds did not become known until a few years ago. In addition, little knowledge is available with respect to measures to be taken on the primary-gas side to abate PCDD/F formation.

For the purpose of controlling dioxin and furan formation, comprehensive tests were carried out at two Waelz kiln units of Berzelius Umwelt-Service (B.U.S AG). (That company became Nordag AG in May 2003). Researchers also attempted to correlate the formation and concentration of PCDD/F with operating parameters of the Waelz kiln plant such as the temperature profile along the off-gas line and the acid/basic mode of operation. The objective was to attain a distinct reduction of the PCDD/F concentration in the raw gas by means of primary measures. In doing so, the effectiveness of the combined filtration and adsorption ("filsorption") stage installed in the Waelz kiln plant of B.U.S Metall GmbH for PCDD/F control was to be improved. Details of the testing are provided in the sidebar. This article describes unique

European conditions and regulations and is especially relevant to the specific plant configurations described.

WAE LZ PROCESS

In order to close the material circle between the steel and the zinc industry, Nordag AG operates four Waelz plants with an installed capacity of about 500,000 t of steel mill flue dust per year. The plants are in Germany, France, and Italy and produce around 100,000 t/y zinc and lead that are returned to the resource cycle. By means of process modifications as well as innovative off-gas technology, the Waelz process can be used to treat other materials containing zinc and lead such as residues from the electroplating industry and waste water treatment, zinc sludge and ashes, and contaminated coke.

The feed materials (i.e., steel mill

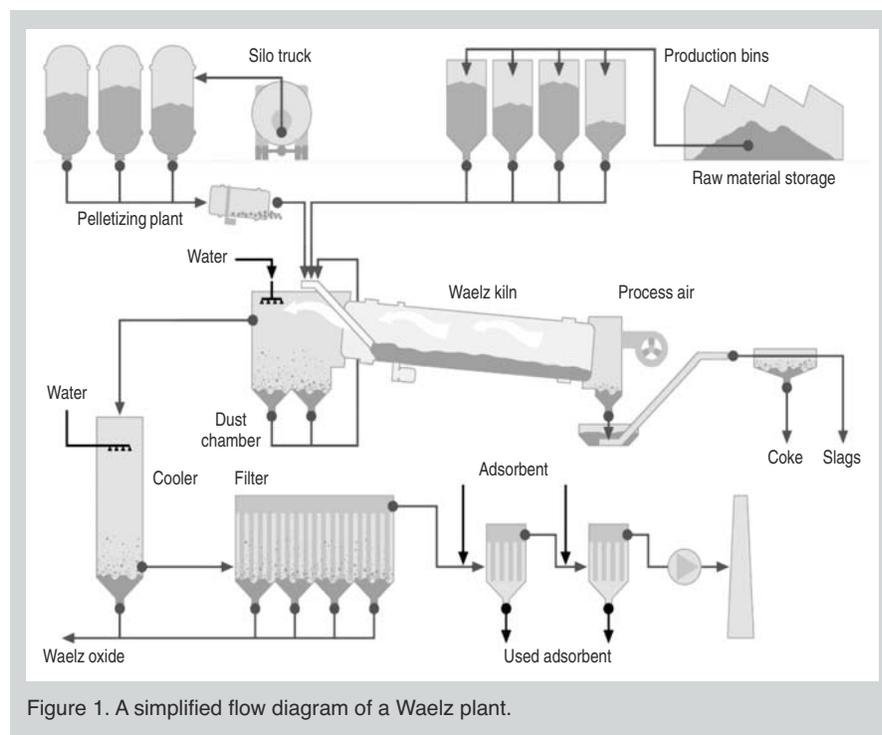


Figure 1. A simplified flow diagram of a Waelz plant.

flue dust, various zinc-bearing residues, coke, and fluxes) are delivered to the plant by road or rail in a dry, consistent, or slacked form. Materials delivered moist (slacked, pelletized), coarse fluxes, and coke are stored in compartments whereas the dry dusts are handled by pneumatic conveying systems and dumped into raw material silos.

To charge the kiln, a homogeneous mix is prepared in pellet form. The Waelz kiln itself is typically 50 m long and has a diameter of 3.6 m. It is slightly inclined and operates at a speed of 1.2 rpm. Figure 1 shows the simplified flow diagram of a Waelz plant.

The pelletized material is moved through the rotary kiln, where it is dried and preheated by kiln gases flowing in countercurrent. In the reaction zone, the metal oxides are reduced at about 1,100°C so that zinc and lead volatilize, emerging from the charge into the gas space in the form of metal vapors. Through controlled admission of air at the kiln outlet end, zinc and lead in the gas phase are oxidized again and the metallic iron content of the charge is re-oxidized and the process heat thus liberated is effectively utilized in the charge. Hence, it is sufficient to add coke at a substoichiometric ratio. Chlorine and alkalis will volatilize jointly with the heavy metals. The dust-laden off-gas is treated in a downstream off-gas unit. In a first stage, the coarse particles—mechanical entrainment due to insufficient pelletizing—are separated in a dust chamber and recycled to the kiln. The hot, dust-laden off-gas is cooled and the Waelz oxide collected in a precipitator. The dust-free off-gas is cleaned of dioxin, mercury, and cadmium to meet local air pollution control regulations and discharged into the atmosphere via a blower.

In the past, Waelz oxide was almost exclusively processed in Imperial Smelting Furnace reactors after briquetting to recover zinc and lead. In light of the worldwide limited capacity of Imperial Smelting plants and the problems inherent in the processing of Waelz oxide because it contains partly high levels of alkalis and halides, B.U.S. developed a two-stage leaching process to directly feed washed Waelz oxide to electrolytic plants for zinc production.²

Depending on the length and rotary

speed of the kiln, the retention time of the feed material in the Waelz kiln is between four and six hours. The Waelz slag, discharged via a wet extraction unit, is a byproduct of the Waelz process and contains all non-volatile components as well as added fluxes. As a function of the Waelz process selected, the slag may be acid or basic. The basicity is used to define the properties of slags, especially in the case of Waelz slag.

The index is defined as:

$$\text{basicity (B)} = \frac{(\% \text{CaO} + \% \text{MgO})}{\% \text{SiO}_2} \quad (1)$$

The acid process in which SiO_2 is added to the mix functions at a basicity of 0.2 to 0.5. The basic process to which lime, limestone, or burnt lime is added is operated at a basicity of between 1.5 and 4. It is difficult to control the operation of a Waelz plant within that range. At a slag basicity of about 1, accretions are forming that may lead to agglomeration in the inlet section of the kiln as well as the formation of iron-rich rings in the reaction zone.

PCDD/F FORMATION IN THE WAE LZ PROCESS

Formation of Polychlorinated Di-benzo Dioxins and Furans

As can be derived from numerous studies,³⁻⁸ the formation reactions

of PCDD/F primarily occur on the surface of process dusts. PCDD/F can be formed by means of two different mechanisms:⁶⁻⁸

- PCDD/F originate from chlorinated cyclical precursor compounds, the so-called pre-dioxins (e.g., chlorinated benzenes, phenols, and polychlorinated bi-phenyls), in the gas phase and heterogeneous reactions on the surface of fly ash particles in a temperature range of 300–800°C.
- Due to the existence of carbon in the filter dusts and/or the organic carbon compounds, a de-novo synthesis of PCDD/F compounds takes place on the dust surface in the presence of chlorine and/or chloride together with the catalytic effect of copper and copper compounds in the low-temperature range of 200–500°C.

Investigations at waste incineration plants have shown that most of the PCDD/PCDF in process dusts and offgases primarily forms in the cooling phase, a phenomenon that allows the conclusion that the PCDD/F formation as de-novo synthesis is dominant. As the conditions for a de-novo synthesis exist in the Waelz process and the process dusts often remain in the offgas system for an extended period of time due to the use of electrostatic precipitators, the re-

THE TESTED WAE LZ KILNS: A DESCRIPTION

B.U.S Metall GmbH

The plant location was established at the MHD Berzelius Duisburg zinc smelter in 1906. Since 1929 a Waelz kiln has been operated on the premises to process residues from the smelter's own operations (zinc-bearing muffle ashes, slag) and materials bought from outside sources. The existing plant has been retrofitted repeatedly in accordance with the state of the art and its feed adjusted to the changes in the zinc-containing residues available. Until March 2001, the Waelz plant was operated in acid mode by the addition of SiO_2 as flux. From March 2001 onward, with the introduction of SDHL¹ technology the plant operation was changed over to the basic mode and the processing capacity thus increased to 80,000 t/y of steel mill flue dust. The off-gas system was not changed.

B.U.S Zinkrecycling Freiberg GmbH

On 3 July 1992, B.U.S AG acquired the Waelz plant in Freiberg/Saxony. Since that time, zinc-containing residues—especially steel mill flue dust—have been processed at the plant. To secure a long-term perspective for the company, the capacity was continuously raised at that location. In November 2000, during a three-month shutdown, the existent kiln was enlarged, the off-gas cooling and cleaning system renewed, and the leaching capacity for Waelz oxide increased. As a result, the processing capacity was boosted to 100,000 t/y of steel mill flue dust. During the entire operating period, the Waelz plant was operated in the basic mode by the addition of lime as flux and the basic concept of the combination of off-gas cooling and cleaning was preserved.

A second kiln with a capacity of 125,000 t/y was started up in Freiberg in September 2002.

COMPARISON OF THE TWO OFF-GAS SYSTEMS

In addition to the off-gas, Waelz oxide is also discharged from the Waelz kiln, imposing distinctly higher demands on the off-gas cleaning systems as compared to those of other metallurgical operations. Up to the point where the product is separated in the downstream product filter, the off-gas features a dust content of about 150–200 g/m³.

When comparing the two off-gas cleaning systems, it becomes obvious that the units are based on different concepts. In particular, regarding the dioxin problems, an important difference is the method of separating the Waelz oxide product. The off-gas is quenched with water and/or air and cooled in indirect coolers. The Waelz oxide itself is removed from the off-gas stream at temperatures between 120°C and 350°C. Either a bag filter or an electrostatic gas cleaning system is applied. Along the off-gas lines, due to the high dust contents certain amounts of process dust occur which, depending on their quality, are either added to the product or recycled to the kiln. An entrained-flow adsorber is arranged downstream of the product filter to clean the dust-free raw gas. Table A provides a detailed overview of the arrangement of the individual process units and the temperature profile along the two off-gas lines.

When comparing the two off-gas plants with respect to their individual cooling levels, it is apparent that at B.U.S Metall the off-gas is cooled in two steps, from about 950°C to 350°C. At 350°C, the Waelz oxide is separated and the off-gas temperature subsequently lowered further to 130°C. At Zinkrecycling Freiberg, by contrast, the off-gas is cooled very fast in three steps, from 950°C to 120°C, before the Waelz oxide is separated in the product filter. When considering the extremely different volume flow rates (see Table B), it becomes evident that the retention time in the critical temperature window for the de-novo synthesis of PCFF/F compounds is longer in the off-gas system of B.U.S Metall, than in the off-gas unit at Zinkrecycling Freiberg.

Table B shows the production characteristics of B.U.S Metall before it was changed over to the basic operating mode as well as the production characteristics and volume flows of the two Waelz plants in the basic mode.

Table A. Individual Units and Temperatures through the Two Off-Gas Systems

	B.U.S Metall		Zinkrecycling Freiberg	
	Units	Temperature (°C) (inlet/outlet)	Units	Temperature (°C) (inlet/outlet)
Cooling system	Dust chamber (Water quench)	~ 950–650	Dust chamber (Water quench)	~ 950–750
	Evaporation cooler (Water quench)	650–350	Mixing chamber (Secondary air quench)	750–340
Filter system Offgas cleaning	Electrostatic precipitator	350–320	Flat-tube cooler (indirect)	340–120
	Tubular cooler (indirect)	320–130	Bag filter	120–110
	Entrained-flow adsorption	130	Entrained-flow adsorption	110
	Blower	120	Blower	110

Table B. Comparison of the Production Characteristics and Off-Gas Volumes of the Two Plants

		B.U.S Metall		Zinkrecycling Freiberg
		Acid	Basic	Basic
Steel mill flue dust processing	t _{wet} /d	180–190	260	340
Waelz oxide production	t _{wet} /d	50–60	75	100
Offgas volume	m ³ /h _{n,dry}	40,000	30,000	75,000

formation of PCDD/F is quite possible in the offgas cleaning phase.

PCDD/F Emissions with Basic and Acid Operating Mode

Table I reflects the typical PCDD/F concentrations for the off-gas and the accruing dusts in the two Waelz kiln plants tested. The relevant chlorine and carbon concentrations are shown with respect to the formation of PCDD/F.

At 50–1,000 ng toxicity equivalent (TE)/m³, the concentrations measured in the raw gas of the Waelz kiln plant of B.U.S Metall in acid operating mode exhibit the highest contents. In basic mode, the PCDD/F content drops significantly to 8–23 ngTE/m³. The PCDD/F concentrations in the raw gas of the Freiberg plant, 1.5–2.1 ngTE/m³, gave the lowest raw gas levels.

As a result of the extremely high

raw gas concentrations measured in the acid mode, the orientative clean-gas specification for the plant of 0.1 ngTE/m³ was not safely maintained despite the two-stage filter sorption stage.

The comparison of the PCDD/F concentrations analyzed in the Waelz oxide dust as well as the laden adsorbent from the filter sorber shows a similar picture. At PCDD/F contents of 140–1,000 µgTE/kg in the laden adsorbent and 900–1,620 ngTE/kg in the Waelz oxide, the PCDD/F solids loads found in acid mode are distinctly above the level of the values determined in the basic mode. By changing over to basic operation, it was possible to reduce the solids load values to 0.5–38 µgTE/kg for the laden adsorbent and 10–30 ngTE/kg for the Waelz oxide.

As mentioned in the preceding section, among other factors the chlorine content exerts a decisive influence on the formation of PCDD/F. The comparison of the chlorine contents measured in the off-gas and in the dust of the Waelz plant, on the one hand, and the PCDD/F concentrations found in each case, on the other, confirms this relationship. The highest chlorine concentrations are found in the case of the acid operating mode. For this reason, the changeover to the basic operating mode is of particular significance for the suppression of the formation of PCDD/F. Various investigations on the suppression of PCDD/F formation in dusts from waste incineration plants have demonstrated that basic substances such as CaO will prevent the formation of these pollutants on dusts. It is assumed that the basic substances react with HCl in the off-gas and thus reduce the chlorine supply needed for PCDD/F formation.

PCDD/F Contents along the Off-Gas Line in the Acid Mode

Concentrations of PCDD/F were determined during a measuring series in the off-gas line of the Waelz kiln plant of B.U.S Metall in acid operating mode.⁹ The measurements were carried out before the changeover of the plant to basic operation to obtain information on the PCDD/F profile along the off-gas line. Based on those findings, suitable PCDD/F abatement strategies were inferred for the Waelz process. The evaluation of the results showed that the

Table I. PCDD/F, Cl, F, and C Contents of Offgas and Filter Dusts

	B.U.S Metall		Zinkrecycling Freiberg
	Acid	Basic	Basic
Clean gas concentrations			
O ₂ content	vol. %	15	12
HCl	mg/m ³ n,dry	< 30	2.5
HF	mg/m ³ n,dry	< 5	< 0.4
PCDD/F	ngTE/m ³ n,dry	1–25*	0.01
Raw gas concentrations (before adsorption stage)			
HCl	mg/m ³ n,dry	< 150	6.5
HF	mg/m ³ n,dry	< 150	< 0.5
PCDD/F	ngTE/m ³ n,dry	50–1,000	8–23
Adsorbent from filtersorption stage**			
Cl	%	7/7***	0.3/0.4***
F	%	12/0.75***	0.1/0.15***
C	%	25/26***	24***
PCDD/F	µgTE/kg	1,000/140***	38/0.5***
Waelz oxide			
PCDD/F	ngTE/kg	900–1,620	10–30
			60–500

* Peak values

** Mean values from available analyses

*** First adsorption stage/second adsorption stage

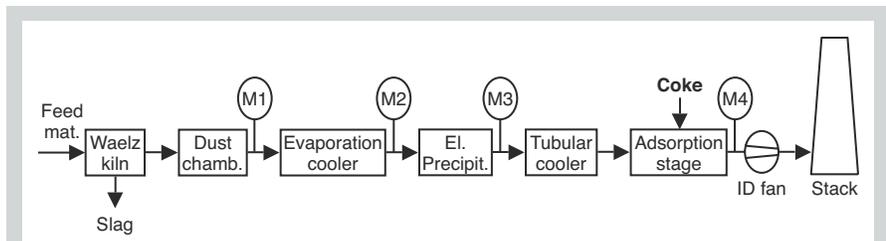


Figure 2. An offgas line with measuring point arrangement.

dust has an extremely high potential for de-novo synthesis of PCDD/F during Waelz kiln operation.

As shown in Figure 2, measuring points were arranged in the gas stream after the dust chamber (M1), after the evaporation cooler (M2), after the electrostatic precipitator (M3), and in the clean gas after the activated-lignite-coke-operated adsorption stage (M4). Due to the high dust content of up to 200 g/m³ at measuring points 1 and 2, these measurements were carried out in derogation of the Association of German Engineers (VDI) code using a sinter metal candle filter installed in the gas stream. This sampling technique led to a falsification of results due to the formation of dioxin/furan on the filter. A brief description of the measuring points with the analysis method applied for the determination of PCDD/F is given in Table II.

Table III shows the results of the measurements along the off-gas line with respect to dioxins/furans, calculated as toxicity equivalents. The measurements were made under normal operating conditions of the Waelz kiln plant.

What is striking is the extremely high PCDD/F concentrations of 598 ng/m³ found at measuring point 1 and 3,695 ng/m³ at measuring point 2. As explained in the following section, these extreme values can be attributed to the high PCDD/F formation potential of the Waelz oxide dusts in combination with the PCDD/F sampling. During measuring, the candle filters in the off-gas stream quickly became covered with a dense dust layer. In the hot atmosphere of the off-gas stream, this dust deposit gave rise to an increase in the PCDD/F contents in the filter as a result of the PCDD/F breeding effect. Consequently, the PCDD/F

concentrations determined at measuring points 1 and 2 do not describe the actual off-gas concentrations. For accurate results, the sampling technique has to be adjusted to the findings about de-novo formation of PCDD/F. When taking samples at temperatures around 300°C it is imperative to cool the gas and flue dust within a matter of seconds to safeguard that no further dioxin synthesis (de novo) takes place on the filter, thus falsifying the result.

A comparison of the PCDD/F concentrations at measuring points 1 and 2 clearly indicates the influence of temperature on the PCDD/F de-novo synthesis. The gas sample taken in the critical temperature window of the de novo synthesis after the evaporation cooler at around 350°C shows, in combination with the high dust load of up to 200 g/m³, the highest PCDD/F content of 3,695 ng/m³.

A PCDD/F content of 68 ngTE/m³ was measured in the offgas stream after the electrostatic precipitator. At a PCDD/F clean gas value of 0.08 ngTE/m³, the effectiveness of the adsorption filter operated with activated lignite coke for separating the APCDD/F passing the filters is confirmed.

PCDD/F Formation on Dusts from the Waelz Process

In order to clarify the origin of PCDD/F formation in the Waelz kiln dust and assess the influence of the mode of operation (acid/basic operation) on the PCDD/F formation potential, dust samples were taken from the dust collectors of the two Waelz kiln lines and analyzed at the Research Center Karlsruhe to determine the so-called de-novo activity.¹⁰ As the temperature after the evaporation cooler of the B.U.S Metall plant and the temperature after the mixing chamber of the Zinkrecycling

Table II. Measuring Point Description and Analysis Method

	M1	M2	M3	M4
Measuring point	After dust chamber	After evaporation cooler	After electrostatic precipitator	After adsorption filter (clean gas)
Temperature	~650°C	~350°C	~320°C	~140°C
Dust content	150–200 g/m ³	150–200g/m ³	5–10 mg/m ³	0.2–2 mg/m ³
Sampling	Sinter metal candle filter, filter openings 2 µm			
Measuring	No measurement as per VDI code		Arrangement conforming to VDI code 2066, sheet 1	
	Measuring acc. to VDI code 3499, sheet 3			
Analysis method	EN 1948, high-resolution gas chromatography/high-resolution mass spectrometry			

Table III. PCDD/F Contents along the Off-Gas Line

Measuring Point	Sampling Period	Mean O ₂ Content (vol.%)	TE Value Unrelated (ng/m ³)	Temperature Sampling Point (°C)
1	16:25–18:36	2.5	598.0*	584
2	11:25–13:35	6.9	3695.0*	354
3	11:30–17:40	6.2	68.0**	270
4	11:35–18:20	13.5	0.08**	119

* Only PCDD/F contents passing the filters (special measurement through sinter-metal candle filter; filter openings 2 mm).

** PCDD/F contents not retained by the filters and bound to particles.

Table IV. PCDD/F Concentrations before and after Thermal Treatment of Waelz Oxide Dust

	B.U.S Metall Acid Kiln Operation Mode (before change-over)				Zinkrecycling Freiberg Basic Kiln Operation Mode			
	Dust Chamber 350°C	Cooler 350°C	Electr. Precipit. 350°C	Electr. Precipit. 270°C*	Dust Chamber 350°C	Mixing Chamber 350°C	Cooler 350°C	Bag Filter 350°C
Dust sample before thermal treatment "original sample" (ng/g)								
Σ PCDD/F	53	31	13	13	11	5	7	29
Gas sample after thermal treatment (ng/g)								
Σ PCDD/F	2,157	3,706	6,676	2,435	203	44	100	134
Dust sample after thermal treatment (ng/g)								
Σ PCDD/F	161	150	82	66	66	5	14	2
Sum of gas and dust samples after thermal treatment (ng/g)								
Σ PCDD/F	2,318	3,856	6,758	2,501	269	49	114	136
Distribution between gas phase and solids (%)								
Gas	93	96	99	97	75	90	88	99
Dust	7	4	1	3	25	10	12	1
Increase Σ PCDD/F (gas/dust sample after treatment/dust sample before treatment)								
Factor	44	124	520	192	24	10	16	5

* Special examination to determine the influence of temperature on PCDD/F formation.

Freiberg plant are comparable at about 350°C, the thermal experiments were carried out at 350°C. The tests were made within the scope of the research project backed by the European Union, "Minimization of Dioxins in Thermal Industrial Processes: Mechanisms, Monitoring and Abatement (Minidip)."¹¹

The samples were heated to 350°C each in a heater through which air was sent for 2 h. The synthetic gas stream (20% O₂ and 80% helium) was captured in a toluene wash bottle at the heater outlet. After the thermal treatment, the solids and the solution from the wash bottle were treated separately and analyzed for PCDD/F. The purpose of the separate treatment of the two matrices was to obtain information on the PCDD/F distribution between solid and gas phases. To gain additional information on the influence of the offgas temperature on PCDD/F formation, a dust sample from the electrostatic precipitator of the B.U.S Metall plant was analyzed at 270°C.

Table IV contains the mean values of the thermal test results. In addition, the PCDD/F concentrations of the original

samples were determined. The PCDD/F concentrations analyzed in the original samples, of 53 ngTE/g in the dust from the dust chamber of the B.U.S Metall plant, exhibited the highest PCDD/F load. The lowest PCDD/F content found in that plant was 13 ngTE/g for the dust from the electrostatic precipitator. Compared to that plant, the PCDD/F contents of the original samples of Zinkrecycling Freiberg plant were lower. At 29 ng/g, the highest PCDD/F concentration was found in the Waelz oxide from the fabric filter.

The thermal treatment of the dust samples resulted in significant increases in the PCDD/F contents. As shown

in Figure 3, the dusts from the B.U.S Metall plant feature the highest activity for the de-novo formation of PCDD/F. The PCDD/F concentrations of the samples from this plant rise by a factor of 44 for the dust from the dust chamber and by a factor of 520 for the dust from the electrostatic precipitator. The de-novo activity of the dusts analyzed from Zinkrecycling Freiberg, by contrast, is distinctly less pronounced. At a factor of 24, the most intensive de-novo formation of PCDD/F was determined in the dust sample from the dust chamber.

The examination of dust from the electrostatic precipitator of B.U.S at 270°C indicates a less distinct tendency toward de-novo synthesis of PCDD/F compared with the experiment at 350°C. The rise in PCDD/F concentration drops from a factor of 520 at 350°C to a factor of 192 at 270°C.

The problems inherent in the affinity to PCDD/F de-novo synthesis in the offgas stream of the plant are heightened by the extreme PCDD/F distribution between solid and gas phase. More than 90% of the newly formed PCDD/F is present in the gas phase. The particle-bound PCDD/F, by contrast, is negligible at a share of less than 10%. It can easily be seen that with dust collection alone a satisfactory improvement of the PCDD/F level cannot be achieved. The abatement of PCDD/F calls for the application of secondary measures (e.g., adsorption on activated coke) or the implementation of measures on the primary-gas side. The latter can be attained, for example, by avoiding extended retention periods of the Waelz oxide dusts in the critical temperature window of the de-novo synthesis.

CONCLUSIONS

The formation of PCDD/F takes place primarily in gas/solids reactions on the

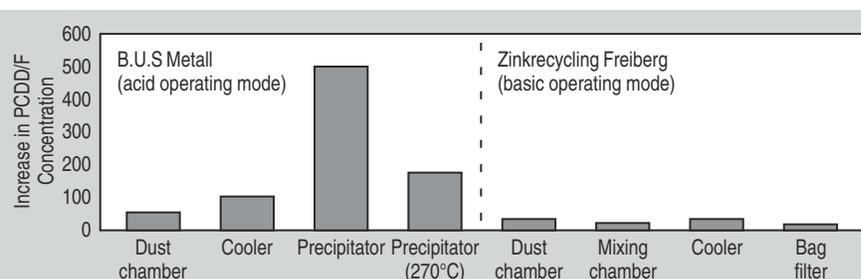


Figure 3. The PCDD/F formation potential (de-novo activity) of various dust types from the Duisburg and Freiberg Waelz kiln plants.

Waelz oxide dust at temperatures around 300°C. From the dependencies shown by the measurements, several possibilities for minimizing the PCDD/F formation can be derived. Extended retention times of major dust amounts in the temperature window of the de-novo synthesis should be avoided. The capture of major dust rates should take place at temperatures below 250°C or above 600°C. In particular, electrostatic precipitators should be operated at offgas temperatures below 250°C in view of the long retention time of the dusts. In addition, the chloride content in the dust and gas should be minimized by a suitable mode of operation of the Waelz kiln plant. The changeover from acid to basic kiln operation implemented at the B.U.S Metall plant shows that by curbing the chlorine load alone a significant PCDD/F minimization formation can be achieved. The existent adsorption stage is thus distinctly relieved. Finally, the PCDD/F concentrations in the feed materials are

almost completely destroyed thermally in the basic operating mode and do not have a significant influence on the raw gas composition.

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