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'DE NOVO' TESTING ON DUSTS COLLECTED IN TWO WAE LZ PROCESS PLANTS – COMPARISON IN DIOXIN EMISSION PROFILE

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Introduction

The Waelz process converts Electric Arc Furnace (EAF) -Dust - zinc, lead and to a minor extent copper bearing iron oxide - arising in the iron and steel industry, into a 'Waelz crude zinc oxide'. The raw material is composed out of heavy metal contaminated iron oxides of various origins. The treatment process is conducted in a high temperature rotary kiln convertor, in which the raw material is moved from the higher feeding side to the lower, slag discharge side, in counter current with hot gases. In the kiln the charge is gradually heated and reduced with coke. The zinc and lead are volatilised and transferred to the gas phase. Above the reducing solid charge atmosphere, however, gas phase conditions are oxidising, so that the volatilised zinc metal fumes are again oxidised to zinc oxide. The gas phase is freed from coarse particulate in a settling chamber, and the coarse dust recycled to the rotary kiln. The finely divided Waelz oxide is carried along by the gas and collected in a baghouse filter.

In total seven samples were taken to be analysed from the off-gas side, from two separate plants. Both the plants have a totally different gas cleaning device. All samples were analysed for each of the following chloroaromatics: PCDD, PCDF, PCBz, PCPh, and PCB.

Table 1: Description from sample location, plant name and slagging mode

Sample	Description / sampling location	Plant	Slagging mode
79	Dust-settling chamber	A	Acidic
80	Cooler	A	Acidic
81	Product filter	A	Acidic
91	Dust-settling chamber	B	Basic
92	Dust-settling chamber	B	Basic
93	Cooler	B	Basic
94	Product filter	B	Basic

Materials and Methods

Materials: The 'de novo' experiments were conducted in a tubular glass reactor (1.5 cm Ø x 50 cm length) mounted vertically in an oven. Dust was placed on a glass frit in the middle of the glass tube and contacted for a time period of 2 hours and a temperature of 270°C for sample 81 and 350°C for all samples with a gas stream of 20 % O₂ in Air (50 ml/min). Volatile chloroaromatics were collected in a toluene impinger. The extract of the dust and the solution of the toluene impinger were cleaned-up and analysed separately.

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Methods: The PCPh, PCBz, PCB and PCDD/F were quantified by the use of ^{13}C -internal standards. The PCPh and PCB were analysed by HRGC/LRMS with a 60 m and PCBz with a 30 m DB-5 column The PCDD/F by HRGC/HRMS (HP5890 - Fisons Autospec) with a 60 m DB-Dioxin column.

Results and Discussion

The samples varied in original I-TEQ and PCDD/F-load over about 1 order of magnitude:

Table 2: Original sample concentrations

	Sample	79	80	81	91	92	93	94
I-TEQ	ng TEQ/g	13.6	0.47	0.17	0.28	0.11	0.10	0.41
PCDD	ng/g	15.9		5.20	1.07	0.63	3.30	7.75
PCDF	ng/g		7.96	7.85	9.99	4.45	4.06	21.2
PCDD/F	ng/g		31.4	13.1	11.1	5.08	7.36	30.0

These are to be compared with:

Table 3: Tentative concentration ranges for comparison

Value	Low	Medium	High	
I-TEQ, ng/g	< 0.1	$0.1 < x < 1$	$1 < x < 10$	> 10
PCDD, ng/g	< 2	$2 < x < 20$	$20 < x < 200$	> 200
PCDF, ng/g	< 3	$3 < x < 30$	$30 < x < 300$	> 300
PCDD/F, ng/g	< 5	$5 < x < 50$	$50 < x < 500$	> 500

There are no standard values for evaluating the dioxin content of dust samples, arising from filter plant in the literature, except for the value of **5 ng/g TEQ** like prescribed in the "Gefahrstoff Verordnung" and the set of values contained in Guidelines on the Dioxin Contaminated Soil.

From the seven samples only one, namely 79, taken in the dustsettling chamber of plant A, has a high concentration for TEQ, PCDF and for the sum of PCDD and PCDF. Another sample has a high level with respect to the PCDD. But the other samples are medium to low in their concentrations of TEQ, PCDD and PCDF.

After annealing, the plant B samples give the following results: the total TEQ-load, i.e. gas phase + solid residue combined, increases by one order of magnitude, but the TEQ-load of the solid residue alone only changes with a factor **0.11 to 5.4**, which basically means a statu quo ante, with final values ranging **0.1 to 1.5 ng TEQ/g**. Annealing mainly generates gas phase TEQ with values ranging from **0.88 to 2.6 ng TEQ/g**, i.e. a multiplier of **6.3 to 24**, which means that most of the TEQ (**63 to 98 %**) is in the gas phase.

Table 4: PCDD values and multipliers overview

Samples	Original Load ng/g	Solid load annealing ng/g	Multiplier (2)/(1)	Gas load anneal. ng/g	Multiplier (3)/(1)	Sum of solid + gas phase ng/g	Multiplier (4)/(1)
Plant A	5.2 to 23.4	14.6 to 85	1.36 to 7.36	291 to 4863	18.3 to 935	314 to 4878	19.7 to 938
Plant B	0.63 to 7.75	0.75 to 7.98	0.10 to 7.48	0.47 to 50	0.44 to 12.6	4.91 to 51.0	6.58 to 14.6
Comparison	A: 3 to 10 times higher	A: 10 to 20 times higher	A: 10 times higher to equal	A: 100 to 500 times higher	A: 45 to 75 times higher	A: 60 to 100 times higher	A: 3 to 60 times higher

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In case of the PCDD, annealing increases the total PCDD by a factor ranging from **6.6 to 14.6** for plant B samples and from **20 to more than 600** for plant A samples. Hence the latter are roughly one order of magnitude more active. Almost all of 'de novo' formed PCDD report to the gas phase (**83-99%**, one exception for 91). Annealing increases the solid phase of the plant A samples by a factor 1.5 to 3; plant B samples vary over a wider range. Decreasing the temperature from 350 °C to 270 °C reduces the 'de novo' activity by a factor larger than **two** for both the total multiplier and the gas phase activity. On the other hand, the residue remains higher loaded at 270 °C by a factor **2.2**, which shows the influence of temperature on the gas/solids partition.

Table 5: PCDF values and multipliers overview

Samples	Original Load ng/g	Solid load annealing ng/g	Multiplier (2)/(1)	Gas load anneal. ng/g	Multiplier (3)/(1)	Sum of solid + gas phase ng/g	Multiplier (4)/(1)
Plant A	7.85 to 36.8	27.9 to 138	3.55 to 15.1	718 to 3763	45.9 to 479	718 to 3826	45.9 to 487
Plant B	4.06 to 21.2	1.04 to 57.6	0.05 to 5.76	39.9 to 203	4.00 to 20.3	43.6 to 261	4.00 to 26.1
Comparison	A: 1.7 to 1.9 times higher	A: 2.4 to 26 times higher	A: 2.6 to 70 times higher	A: 18 times higher	A: 11 to 24 times higher	A: 15 times higher	A: 11 to 20 times higher

Annealing increases the PCDF by 4.0 to 26.1 for plant B and from 50 to more than 400 for plant A. Hence the plant A samples again are one order of magnitude more active. As for PCDD, almost all 'de novo' formed PCDF report to the gas phase (**92-98%**). Annealing increases the solids loading for plant A by a factor **3.55 to 15**, whereas the plant B samples again vary over a wider range, but also tend to remain lower in PCDF. Decreasing the temperature from 350 °C to 270 °C reduces the 'de novo' activity by a factor larger than **four**, i.e. more than the PCDD. Also, the residue decreases at 270 °C, by a factor of **2.2**.

Table 6: PCBz values and multipliers overview

Samples	Original Load ng/g	Solid load annealing ng/g	Multiplier (2)/(1)	Gas load anneal. ng/g	Multiplier (3)/(1)	Sum of solid + gas phase ng/g	Multiplier (4)/(1)
Plant A	16.8 to 238	30.7 to 425	1.49 to 17.4	10168 to 25169	104 to 1355	10460 to 25593	105 to 1357
Plant B	3.90 to 381	n.d.	n.d.	3682 to 32728	34.0 to 1595	3682 to 32728	34.0 to 1595
Comparison	A: 4 higher and 1.6 times lower	-	-	A: 3 times higher and 1.3 times lower	A: 1.2 to 3 times higher	A: 3 times higher and 1.3 times lower	A: 1.2 to 3 times higher

Annealing increases PCBz by **34 to almost 1600** for plant B and from **100 to about 1300** for plant A. Almost all reports to the gas phase (**97-99.5%**), but the PCBz of the solid phase of the plant A samples rises by a factor **1.8 to 3.8**. Decreasing the temperature from 350 °C to 270 °C reduces the 'de novo' activity by a factor of about **two**, i.e. more or less like the PCDD, for both the total multiplier and the gas phase, but the PCBz-load of the residue at 270 °C increases by a factor of 7.

Annealing increases the total PCPh by **1.2 to almost 12** for plant B and **3 to almost 70** for plant A; almost all reports to the gas phase (**96-99%**). The solids load multipliers are **0.03 to 0.90** for plant A; from **0.09 to 5** for plant B. Decreasing the temperature from 350 °C to 270 °C reduces the 'de novo' activity by a factor of about **two** for the total multiplier and the gas phase activity.

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Table 7: PCPh values and multipliers overview

Samples	Original Load ng /g	Solid load annealing ng /g	Multiplier (2)/(1)	Gas load anneal. ng /g	Multiplier (3)/(1)	Sum of solid + gas phase ng /g	Multiplier (4)/(1)
Plant A	397 to 453	11.5 to 429	0.03 to 1.08	1149 to 26470	4.14 to 66.6	1175 to 26481	2.96 to 66.6
Plant B	2.26 to 24.6	2.29 to 15.6	0.09 to 4.96	5.89 to 66.5	1.10 to 9.34	17.1 to 82.1	1.19 to 11.5
Comparison	A: 8 to 175 times higher	A: 4 to 28 times higher	A: 3 to 5 times lower	A: 195 to 400 times higher	A: 4 to 6 times higher	A: 70 to 322 times higher	A: 2.5 to 6 times higher

Table 8: PCB values and multipliers overview

Samples	Original Load ng /g	Solid load annealing ng /g	Multiplier (2)/(1)	Gas load anneal. ng /g	Multiplier (3)/(1)	Sum of solid + gas phase ng /g	Multiplier (4)/(1)
Plant A	88.0 to 130	45.6 to 68.3	0.35 to 0.78	54.6 to 579	0.60 to 6.36	101 to 632	1.11 to 6.94
Plant B	10.3 to 20.1	121 to 147	6.69 to 13.1	79.6 to 411	3.96 to 36.8	210 to 558	10.6 to 49.9
Comparison	A: 6.5 to 8.8 times higher	A: 2.2 to 2.7 times lower	A: 16 to 20 times lower	A: 1.3 lower - 1.5 times higher	A: 6 times lower	A: 2 higher to 1.2 times lower	A: 7 to 10 times lower

Annealing increases total PCB by **10.6 to almost 50** for plant B and by **1.1 to 7** for plant A, with the major part in the gas phase (**65-85%**). Plant B samples are more active. Annealing reduces the solid phase PCB by a factor **2** in plant A; the plant B samples increase **7 to 10 times**. Decreasing the temperature from 350 °C to 270 °C reduces the 'de novo' activity by a factor of **three**.

In all cases, most of the PCDD, PCDF, PCBz, PCPh, and PCB after annealing were to be found in the gas phase. The samples from plant A are rather more active, which is possibly related to the acidic operating mode of this plant. In earlier lab testing, caustic materials such as NaOH, Ca(OH)₂ were identified to be potent inhibitors.

The values for the ratio PCDD/PCDF are higher than expected for metallurgical samples, especially for plant A. The spread on these values is relatively large, and an ascending trend ratio along the path was found. Annealing decreases the PCDD/PCDF-ratio for upstream samples and increases it for downstream ones (81, 94). In plant A, the gas phase has a higher PCDD/PCDF-ratio than the solid phase, which is surprising given their relative volatility.

It is believed that a study of the gas/particle phase distribution is important in deciding upon the potential effect of particle filtration and waste gas temperature to reduce the TEQ-load of process gases.

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References

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