ANALYSIS AND SOLUTION OF DIOXIN PROBLEMS IN A MANGANESE ORE SINTERING PLANT

Peter Brown[1], David Hassell[1], Kathleen Schroyens[2], Nadezhda Zyaykina[2] and Alfons Buekens[2]

[1] Tasmanian Electro Metallurgical Co., PO Box 164, George Town Tasmania 7253, Australia
[2] Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium, E-mail: abuekens@vub.ac.be

Introduction

In 1977 Olie et al.[1] discovered dioxins on fly ash of Municipal Solid Waste (MSW) incinerators. Only much later[2] dioxins were found in off-gases from iron ore sintering plant. This source even becomes the most important one in countries with large integrated iron & steel plants, as emissions from MSW- and Hospital Waste Incinerators are being curtailed below a limit value of 0.1 ng I-TEQ/Nm^3. Raw gas levels in individual sintering plants vary typically from 0.5 to 20 ng I-TEQ/Nm^3. In Japan the Ironmaking Committee of the Joint Research Society, ISIJ, commissioned several studies[3]. In Germany, Dr. Putz[4] simulated the process using a sintering pot. MINIDIP[5] conducted numerous *de novo* lab-scale tests and tested Jet REMPI techniques for identifying the first steps in the 'de novo' dioxin process at Deutsche Luft- und Raumfahrt (Stuttgart). Xhrouet et al.[6] conducted 'de novo' and inhibition studies. Kasai[3] tested the effect of many parameters.

In 1996 dioxins were discovered in off-gases from an MnO_2 ore fines sintering plant at Bell Bay in Tasmania. The local community and regulators are immediately advised of the presence of dioxins and results of an independent health risk assessment showed that risk was acceptable, according to U.S. EPA criteria. As part of a proactive improvement policy, TEMCO conducted further work with the aim of a substantial reduction in emissions. Dioxin emissions were unexpected and had never been described before in this system. TEMCO considered and tested various methods for reducing dioxin emissions by suitably combining primary and secondary measures, and has been most successful in doing so. The potency of the process, so lean in chloride that Cu and Zn are hardly volatile, is tentatively ascribed to the strongly oxidising characteristics of MnO_2 ore fines, but tests and studies are still ongoing, since the reason for the original emission remains unclear.

Methods and Materials

TEMCO produces about 100,000 tonnes per year ferromanganese and the same amount of silico-manganese in electric furnaces, consuming about 200,000 tonnes per year of manganese ore fines (Table 1-3). Sinter and other raw materials are fed to submerged arc furnaces and smelted to alloy that is cast and sized to customer requirements. The Sinter Plant is a Lurgi machine installed in 1976, with a 36 m^2 strand area, 2 m wide and 18 m long. The hearth layer is 50 mm thick and the total bed depth 500 mm. The strand speed, formerly 0.7 m/min with residence times of 20 min in the baking section, 5 min in the cooling section, later increased to 0.85 m/min. Sinter cooling continues on steel discharge conveyor belts. Manganese ore fines are supplied from a mine in the Northern Territory. Coke breeze is sourced mainly from OneSteel Whyalla works (South Australia). Spillage (largely manganese ore fines but including coke and coal) is collected around the Sinter Plant and returned to the process. Off gas is cleaned in an electrostatic precipitator (ESP), cooling gas in multiclones. The dust (Tables 4-7) also returns to the feed. Igniting coke breeze in the top of the burden starts sintering of ores, based on forming complex manganese/iron

silicates. A hot reactive seam is aspired downward through the layer until the hearth layer is reached and cooling starts. The process requires precise control of the coke and moisture contents of the mix. Return fines, undersized sinter, are added to the mix at 12 to 20 %. Coke breeze supplies Carbon (Fixed C, 82.5 %), Volatile Organics (2.8 %) and almost all sulphur to the system. The latter is important, since a statistical correlation is found between dioxins and sulphur, which can probably be interpreted as one with coke. Coke ash reports largely to the sinter. For sure, coke plays a central role in dioxin generation, but it is unclear how far either the coke proper or the evolving tars and volatiles are responsible. Very important elements are chlorine, copper, lead, and sulphur. Given the very low levels of chlorine in all raw materials the availability of chloride is presumably rate determining, so that the discarding of fines from the ESP, enriched in chlorides, could be of some help. Also the traditional catalyst, copper, is not so widespread in the system and lead is not supposed to be a good catalyst. Hence, the presence of an appropriate catalytic system may also be rate determining. The levels of Cu, Pb, and Zn of ore fines and coke ash seem similar (Table 4) which means that the ore fines (ca. 50 tph) are a more important supplier than the coke breeze (only ca. 5 tph). Table 6 compares TEMCO dust with that from iron ore sintering, a plant with similar original emission levels. It is really surprising seeing TEMCO reach similar dioxin levels with both chlorine and copper one or two orders of magnitude lower.

The TEMCO/VUB study strategy for solving the dioxin problems is based upon:
1) A sequential programme of **full plant tests**, designed for reducing the high cost of in-plant dioxins sampling & analysis and taking into account the restrictions in varying operating conditions, feed composition, the limited measurement and monitoring facilities, and inherent variability regarding raw materials and process conditions,
2) Designing and conducting **'de novo'** tests, involving TGA (Thermo Gravimetric Analysis), combined with evolved gas analysis (MS, sample collection, followed by thermal desorption and GC-MS analysis) or DSC screening of samples (Differential Scanning Calorimetry).
3) A thorough **characterisation** of dust, originating from baking and cooling sections of the belt, including its content of adsorbed organics and catalytic metals.
4) Various simulations, thermodynamic computations and mass balances.

The full plant trials primarily aimed at testing the reduction measures proposed and supported by analyses and lab tests. A dioxins emissions reduction strategy is devised, considering:
a) *Primary measures*, including int. al.
   (1) **Inhibition**, by addition of urea, amines, sulphur, or strong bases including NaOH and lime, or by steam addition,
   (2) Interrupting **filter dust recycling**, by changing the direction of a moving belt,
   (3) Using **anthracite** or even activated coke instead of coke,
   (4) Providing **coarse** (e.g. 0.5 to 2 mm) rather than fine coke,
b) *Secondary measures*, including
   (1) **Adsorption** or condensation of dioxins and precursors in the coarse hearth layer, down on the belt. Apparently, breakthrough of dioxins from the burden is accelerated by the relatively low moisture content of the burden,
   (2) **Activated carbon** or **lignite coke injection**, perhaps at a level of only 20 – 50 mg/Nm^3.

Results and Discussion
First sampling in September 1996 revealed a total emission of 15 g I-TEQ/yr made up of 17 ng I-TEQ/Nm^3 in the Waste Gas Stack and 19 ng I-TEQ/Nm^3 in the Cooling Gas Stack. In February 1998 the off-gas from wind box 7 is redirected from the Cooling Gas Stack to the Waste Gas

Stack, joining the off-gas from wind boxes 1 to 6. Spillage is removed. In February 1999 the emissions had dropped to 10 g I-TEQ/yr. Since, there has been a further 30 % reduction in emissions as a result of a rising productivity and reduced operating time. As usual, the mere fact of studying plant performance and its relation to emissions had a most beneficial effect and, with the addition of a suitable inhibitor, the present emissions are routinely held below 0.5 g I-TEQ/yr. Detailed sampling has been performed in December 1999, August 2000, March 2001, March/April and July/August 2002, and the results studied together with VUB. The effect of feed and operating parameters are investigated, and their levels correlated with dioxin emissions. An excellent relationship between PCDD/F, PCBz, and I-TEQ is established, most monitoring currently centers on PCBz, so volatile that the PCBz-contribution of dust remaining in the clean gas is uncritical. Moreover, PCBz concentrations are higher than those of PCDD/F and the number of congeners is smaller. Filter dust recycling is stopped at two occasions, leading in both to a vast decrease of lead-in-dust. The concentrations of Cu, Zn and even Cl, are barely affected. It is difficult to avoid outliers in such experiments, since dust collection and sampling is not necessarily reproducible: direct dust sampling from the gas is sometimes spoiled by the considerable under pressure in the ESP, giving rise to elutriation of fines, or dilution with ambient air, whereas dust collected from the ESP has had a variable residence time, linked to the time of rapping collector plates. Much attention is paid to a detailed analysis of dust and its intrinsic correlations between the concentrations of various chemical elements and, those of PCDD/F, PCB, PCBz, PCPh, and PAH (Table 7). *Statistical Analyses.* Dust parameters show often a very strong mutual correlation: Pb is strongly associated with P, K, S, less with Na, Fe. Chlorine rarely appears in the analyses, since its low levels render a precise analysis impossible. Volatiles are associated with C, also with K, P, and S; and negatively with $Si < Ti < Mg < Ca < Fe$. The most potent factor found in forming Dioxins, PCBs and Aromatics is Pb, followed by K, volatiles, P, and strangely enough, sulphur. PCDD/F, 23478-PeCDF, OCDD and OCDF are all strongly correlated with I-TEQ values, whereas PCB-TEQ and PAH correlate fairly.

Conclusions

The dioxins problem in off-gases from an MnO_2 ore fines sintering plant at Bell Bay in Tasmania is entirely unexpected, for the system is so lean in chloride that Cu and Zn, K and Na are hardly volatile, hence fail to enrich markedly in filter dust, albeit steadily recycled. After steady and comprehensive effort it has been possibly to reduce original emissions by a factor of ca. 40.

Acknowledgements

References

1. Olie, K.; Vermeulen, P.L.; Hutzinger, O. (1977) *Chemosphere* <u>6</u>, 455-459.
2. Lahl, U. (1993) *Organohalogen compounds* <u>11</u>, 311-314.
3. Kasai, E. (2003) *Bulletin of the Iron and Steel Institute of Japan (Ferrum)* Vol. <u>8</u>, No. 2.
4. Pütz, R., "Dioxinproblematik bei metallurgischen Prozessen der Stahlindustrie - am Beispiel der Eisenerzsinterung" – Thesis.
5. E.U.-Project MINIDIP "Minimization of Dioxins in Thermal Industrial Processes:

Mechanisms, Monitoring and Abatement", contract n° ENV4-CT97-0587. *Final report*, 2002.
6. Xhrouet, C.; Nadin, C.; Pirard, C., De Pauw, E. (2001) *Environmental Science and Technology* Vol. <u>35</u>, No. 8, pp. 1616-23

Table 1. Feed rates of the various Feed Components, tph and Wt. % ([*]ESP; [**]Multiclone)

Component	Ore Fines	Spillage	Coke	Return Fines	Dust recycle	Sum
Amount, tph	50 - 55	0 - 3.5	4.5 – 5	12	0.013[*] + 0.0075[**]	66 – 75
Amount, wt. %	70.4 - 77.5	0 - 4.9	6.3 - 7.0	16.9	0.018[*] + 0.011[**]	100

Table 2. Granulometric Analysis of the Manganese Ore Fines

Screen Size, mm	> 11.2	> 9.5	> 8.0	> 6.7	> 3.35	> 1	> 0.5	< 0.5
Amount, Wt. %	8	5	8	7	34	34	2	2

Table 3. Coke Ash and Ore Composition Data (Source: Analyses Trials March 2002)

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	BaO	Sum
Coke Ash	0.19	1.08	27.07	50.33	0.510	1.17	3.75	1.19	0.47	8.29	<0.01	94.05
Ore Fines	0.23	0.1	4.20	5.41	0.160	0.94	0.06	0.19	63.60	6.53	0.99	82.41

Table 4. Chlorine, Copper, and Sulphur in the Feed Components

Element	Cu, ppm	Pb, ppm	Zn, ppm	Cl, ppm	S, % or ppm
Ore Fines	4 – 26	9 – 14	6.8 – 75	< 5 – 113	32 – 210
Coke*	6 – 14	5 – 119	14 – 42	< 7	0.5 – 0.6 %
Sinter	52 – 58	41 – 57	116 – 141	7	200 – 1,930
Filter Dust	39 – 130	1700 – 5400	110 – 770	213	1.9 – 3.4 %

*Ash basis = 100, 13 – 14.7 % of the Coke

Table 5. Organics detected in ESP Dust

Location	Field 2 Plates	Field 1 Plates
Dichloromethane soluble matter	4.4	9.4
Total chromatographable matter	0.2	0.3
Sat + Unsaturated C14-C40	0.1	0.2
PAH and other aromatics	0.1	0.1
Other high molecular weight organic matter	4.2	9.1

Table 6. Dust Composition of Iron Ore Sintering plant with similar Emission Levels

	Iron Ore Sintering Plant			TEMCO ESP Dust (Field 1 + 2, combined)		
	Field 1	Field 2	Field 3	Sept. 1996	March 2002	July 2002
Pb	1.1	3.5	10.6	0.17 – 0.54	D.L. – 1.29	0.02 – 0.65
Cl	8.8	21.2	31.6	0.2 - 1	0.1 – 1.3	0.13 – 0.39
K	4.75	13.48	19.5	2.0 – 12	1.1 – 6.4	1.2 – 8.8
Cu	0.04	0.17	0.29	0.007 – 0.013	< D. L.	0.003 – 0.005

Table 7. Quality of Correlations of PCDD/F and PCB with filter dust composition

Class of Compounds	R²>0.85	R²>0.65	R²>0.35	R²< -0.35	R²< -0.65	R²< -0.85
Dx TEQ	Pb, K	Vol, P, S	C, Na		Ti, Mg, Ca	Fe, Si
23478 PeCDF	Pb	K, Vol, P, S	C, Na	Ca	Ti, Si, Mg	Fe
OCDD/F	Pb, K	Vol, P, S	C, Na	Mg, Ca	Si, Ti	Fe
PCB TEQ	Pb, K, P	Vol, P, S	Vol, Na	Mg, Ca	Si, Fe, Ti	
SUM of 16 US EPA	Pb, Vol	K, P, S	C, Na		Ti, Si, Mg, Ca	Fe

Vol = Volatile Matter. The elements Pb, K, P, S strongly enrich in dust fines.