

THERMODYNAMIC ASPECTS OF DIOXIN FORMATION CATALYSIS IN AN MnO₂ ORE SINTERING PLANT

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Introduction

Dioxins are formed in many metallurgical processes, including the sintering of MnO₂ ore fines. Important factors are: the presence of chlorides, oxygen, and carbonaceous materials, speciation and amount of catalytic metals (mainly Cu or Fe). In earlier work^{1,2} the role of volatilisation and eventual condensation of Cu, Pb, Zn, K, Na, ... chlorides was highlighted in dioxin formation.

The typical composition of ore fines, coke (ash) and filter dust is shown in Table 1. Representative sinter samples were mounted, polished and examined by CSIRO³ using a reflecting optical microscope. The main mineral was either hausmannite (Mn₃O₄) or manganosite (MnO) suspended in a eutectic glass matrix with resolved laths of fayalite-Fe₂SiO₄/tephroite-Mn₂SiO₄. However, entrained and deposited dust, enriched in chloride and catalyst, is much more active in dioxin formation than the bulk feed or sinter streams. Minidip studies⁴ demonstrated a lack of activity of feed mix in iron ore sintering and Xhrouet⁵ and Kasai⁶ reach the same conclusion.

The Temco sintering system is characterised by a low chloride filter dust (< 1 wt. %), and hence reduced heavy metal volatility. Coke particles are rather inactive (**DSC test** shows oxidation starting at 350 °C only). For a better understanding of dioxin generation some thermodynamic computations are performed and compared to actual field data, obtained during two test campaigns in which dust recycling was halted. A statistical analysis is made on the enrichment of elements in the dust phase, compared to original ore fines or sinter. The purpose of this work is explaining the genesis of **catalytic systems** for dioxin generation in this specific sintering process, as well as possibilities for their eventual inhibition.

Methods and Materials

Thermodynamic Computations are made in order to establish stable speciation states of Cu, Pb, and Zn during preheating and sintering MnO₂ ore fines. The simulation system was based on the actual composition of ore fines, with very low concentrations of Cu, Pb, Zn, Cl, and S. Especially Cl was low, both in ore and coke ash. Both oxidising and (locally) reducing conditions, and also possible interactions with ore and sinter matrix are considered. Temperature, Cl and S-values are handled as parameters. The latter are not known with precision, given their low values and the difficult representative sampling under industrial process conditions. Software for thermodynamic calculation is **FactSage**.

The speciation of Cu, Zn, and Pb was computed for temperatures of 500 to 1200 °C in steps of 100 °C, assuming interactions with sinter, or not. Results are confronted with those of chemical analysis. Regression analysis on ESP-dust establishes the quality of statistical correlations between various elements and dioxin, PCB, PCBz, PAH. Dust samples are analysed using X-ray fluorescence analysis (XRF) and Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS).

Results and Discussion

Manganese Ores:

The phase transition temperatures of MnO₂ pyrolusite[s1] into Mn₂O₃ braunite[s1], Mn₃O₄[s1] and [s2], and MnO[s1] are predicted in pure air as 465, 877, 1172, and 1536 °C, but vary with gas composition (O₂ and SO₂-content). The result is consistent with the CSIRO study identifying hausmannite (Mn₃O₄) and manganosite (MnO) phases in the sinter.

Metal Volatilisation under oxidising conditions:

In the presence of HCl Pb completely volatilises at 800 – 900 °C as PbCl₂, PbO, and PbCl, in a ratio depending on the HCl concentration. Limited availability of HCl restricts the appearance of volatile Cu and Zn-chloride. Stable forms of **Cu** are (at rising temperature and for 20 mg/Nm³ HCl): CuSO₄ up to 500 °C, CuO.CuSO₄ at 600 °C, converting into CuO tenorite and 0.03 % CuCl[g] at 700 °C. The volatile Cu-fraction continuously rises with temperature attaining 9, 45 and 100 % at 1200 °C (for 2, 20, 200 mg/Nm³ HCl as a parameter). Thus, the presence of chlorides is a limiting step in the volatilisation of copper. Likewise, the stable form of **Zn** at low temperature is ZnSO₄. Above 600 °C complete conversion of sulphate into ZnO zincite takes place. Very little ZnCl₂ [g] is formed. Zinc metal vapour appears from 1000 °C upwards (Table 3); its concentration is independent of the HCl content in the gases.

Chlorine:

At temperatures relevant in dioxin formation (<below 500°C) HCl in the presence of MnO₂ readily converts into elementary chlorine, a most potent chlorinating agent, and in MnCl₂. More chlorine is predicted in case concentrations of HCl, O₂ and oxidants are higher, those of H₂O and reducing agents (including SO₂) are lower, as usual for the Deacon equilibrium.

Influence of SO₂:

Decomposition of CuSO₄ or ZnSO₄ proceeds at lower temperature, when the SO₂ concentration decreases. The same holds for Pb, but volatility of both chloride and oxide are enhanced in the absence of SO₂. This effect is only marginal for Cu and Zn.

Reaction with the Solid Phase:

Under the process conditions, no Cu-, Pb-, or Zn-silicate is stable thermodynamically. The formation of spinels (Al-Fe-Ni-Zn-O) and ferrites, however, deserves special consideration for each metal separately:

Cu. (CuO)(Fe₂O₃) replaces copper sulphate and oxides as stable phase, reducing Cu volatility under its various forms (Table 2, last line).

Pb. (PbO)(Al₂O₃)₆ becomes the stable compound at 600 and 700 °C, but lead volatility is unaltered.

Zn. A series of stable spinels arises, e.g. ZnFe_2O_4 , ZnAl_2O_4 , $\text{Zn}_3\text{O}_4^{2-}$, $\text{ZnFe}_2\text{O}_4^{2-}$, $\text{FeZn}_2\text{O}_4^-$, ZnO_4^{6-} , and reduces the low volatility even more. See Table 3, last line.

Mo. Analysing dust it was found enriched in Mo and P. The first already volatilises at 500 °C, as $\text{O}_2\text{Mo}(\text{OH})_2$. Volatilisation is complete at 1000 °C, in part as MoO_3 di-, tri-, and tetramers.

Table 1. Typical Composition of Manganese Ore Fines (wt. %).

SAMPLE	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Mn
Ore Fines 6/3/02	0.23	0.1	4.20	5.41	0.160	0.94	0.06	0.19	49.25
	Fe	BaO	C	S	Cu (ppm)	Pb (ppm)	Zn (ppm)	Cl (ppm)	
	4.57	0.99	0.0590	0.0032	26.40	9.36	74.52	113.0	

Table 2. Equilibrium calculations on the forms of Cu, Zn and Pb at 20 mg/Nm³ HCl and 800mg/Nm³ SO₂. Part I. Volatilisation of Copper Compounds (mol%).

Compound	700 °C	800 °C	900 °C	1000 °C	1100 °C	1200 °C
CuO_tenorite[s1]	99.97	99.65	97.62	89.08	-	-
Cu ₂ O[s1]	-	-	-	-	75.10	54.98
CuCl[g]	0.03	0.35	2.38	10.89	24.47	40.09
Cu[g]	-	-	-	0.02	0.39	4.54
CuO[g]	-	-	-	-	0.04	0.39
Gas Phase Cu	0.03	0.35	2.38	10.89	24.90	45.02
Idem, Cu-ferrite formed	-	0.02	0.09	0.38	1.28	6.44

Table 3. Part II. Volatilisation of Zinc Compounds (mol%).

Compound	1000 °C	1100 °C	1200 °C
ZnO_zincite[s1]	99.94	99.46	91.8
Zn[g]	0.02	0.51	8.18
ZnCl ₂ [g]	0.04	0.03	0.02
Gas Phase Zn	0.06	0.54	8.20
Gas Phase Zn (Spinel formed)	-	0.04	0.97

Table 4. Part III. Volatilisation of Lead Compounds (mol%).

Compound	700 °C	800 °C	900 °C	1000 °C	1100 °C	1200 °C
PbSO ₄ _anglesite[s1]	99.94	85.99	-	-	-	-
PbO[g]	0.01	12.20	98.83	99.77	99.86	99.80
PbCl ₂ [g]	0.04	1.75	0.94	0.08	0.01	0.01
PbCl[g]	-	0.05	0.23	0.12	0.07	0.03
Pb[g]	-	-	-	0.02	0.07	0.16
Gas Phase Pb	0.05	14.0	100	100	100	100

Reducing conditions:

In the off-gas from the sintering belt there is considerable carbon monoxide (20 – 30 g/Nm³). Reducing conditions are likely to occur in the bed, promoting a deep change in speciation. Copper becomes less volatile, but formation of zinc vapour is now favoured. New solid sulphide species appear, e.g. Cu_2S (for Cu there is no gas phase for $T < 800$ °C). Stable Zn-phases are: ZnS sphalerite; Zn[g] appears only at $T > 600$ °C and it is the only species present at $T > 800$ °C.

Lead is highly volatile, even as PbS[g]: at 700 °C there is only vapour, with 58.0 mol% PbS, 40.6 mol% Pb, 1.37 mol% PbCl, 0.01 mol% PbCl₂. Above 800 °C there is mainly Pb and PbS, with traces of PbO, PbCl, and PbH. Hence, HCl is non-essential in Pb volatility!

Phosphorus is present in coke and was found enriching in dust: it is highly volatile under reducing conditions (100 % at 600 °C) as (P₂O₃)₂[g]. Oxidizing conditions fix P as AlPO₄ and FePO₄. On the other hand, reducing conditions immobilize volatile Mo as, int. al MoS₂ and MoO₂.

Dust concentration values. Statistical Evaluation:

Cross-correlating elementary concentrations in filter dust, ore fines, sinter, and coke ash shows that some elements strongly **accumulate in dust fines**, namely Pb, K, P, and S, whereas Cu, Zn, and – surprisingly – Cl do not enrich in filter dust fines as much as expected from earlier study². Dioxins-in-dust correlate well with all elements from the first group.

During a TEMCO testing programme the **recycling of filter dust** was twice halted for some days, and the resulting evolution in heavy metal concentration monitored. This confirms the above analysis.

Conclusions

Thermodynamic computations are performed, establishing a framework for explaining the genesis of catalytic systems responsible for dioxin generation in MnO₂ ore sintering. This study explains why Pb, P, Mo enrich in fine ESP dust, and Cu or Zn do not as much as expected.

The volatility of Cu, the best catalyst, is limited by low chloride availability, locally reducing conditions, and formation of copper ferrites. Zn is barely volatile, because of low chloride and spinel formation, but reducing conditions assist in volatilizing the metal. Low availability of chloride or reducing conditions are no obstacles for Pb, enriching in dust. P is present in coke and thus likely to experience volatilizing reducing conditions. The role of Mo, under oxidising conditions a very volatile and also a catalytic metal is at present being further tested.

References

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