

Thermodynamic and Kinetic Studies of Dioxin Formation and Emissions from Power Boilers Burning Salt-Laden Wood Waste

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Introduction

Researchers at the Pulp and Paper Institute of Canada found that power boilers burning salt-laden bark, or hogged fuel, could be a significant source of dioxins and furans¹. Subsequently, stack dioxin emissions from 8 full-scale power boilers were measured under a variety of operating conditions. Dioxin emissions ranged from 0.01 to 2.8 ng TEQ/m³ at 11% O₂^{2,3}. Improving combustion conditions in the furnace and lowering ESP temperatures could significantly reduce dioxin/furan emissions. These data were consistent with the results of Kilgroe⁴ and Everaert and Baeyens⁵. Further analysis indicated that the main formation mechanisms proposed in the literature for solid waste incinerators, i.e. precursor and de novo, may also be applied to hog fuel boilers.

The existing literature on dioxin and furan formation in other combustion processes was carefully reviewed. Tan *et al.*⁶ indicated that thermodynamically, PCDD/Fs cannot exist in any significant quantities in oxidizing combustion processes, but may be formed as intermediate products with trace concentrations. The intermediate products could become “permanent” if the reaction conditions kinetically inhibit their subsequent, complete oxidation.

Wikstrom *et al.*⁷ investigated PCDD/F formation in the combustion of an artificial fuel with PVC or CaCl₂ added. They found no correlation between the levels of dioxin formation and the fuel chlorine content. However, Yasuhara *et al.*⁸ observed increases in dioxin formation with the NaCl content when impregnated newspapers were incinerated. In power boilers burning salt-laden hog fuel, the chlorine is introduced mainly as NaCl. To our knowledge, high temperature salt chemistry and its influence on dioxin formation in combustion and thermal processes have not been thoroughly studied. A thermodynamic analysis of the salt chemistry will be provided in this paper.

Though largely empirical⁹⁻¹¹, most of the kinetic models developed to describe PCDD/F formation rates are complicated, containing 8 - 12 parameters that need to be estimated. Everaert and Baeyens⁵ reported a very simple correlation between stack PCDD/F emissions and the electrostatic precipitator (ESP) temperature: $\log(\text{PCDD/F})_T = (0.016T - 3.001)$. Although this correlation cannot quantitatively predict dioxin emissions measured on the Canadian west coastal power boilers burning salt-laden hog fuel², the effect of ESP temperature given in the correlation agrees qualitatively. In this work, we will attempt to develop a semi-empirical model based upon both thermodynamic analysis and kinetic considerations.

Experimental

The experiments, based on which our kinetic model was developed and verified, were conducted on 8 full-scale grate or bubbling fluidized bed power boilers burning salt-laden hog fuel, operating at coastal pulp mills^{2,3}. A typical hog boiler consists of a combustion furnace, steam superheaters, a generating bank, an economizer, an air heater, multicyclones, electrostatic precipitators (ESP) or scrubbers, and a stack. Dioxin emission tests were conducted at the stack. Sludge from waste water treatment was burnt in most of the hog boilers. Hog fuel contained 0.06-2.2% NaCl and 49-66% moisture. Additional details on the boiler designs and operations are provided in other reports^{1,2,3}.

Thermodynamic Analysis

Both organic chlorine (e.g. PVC) and inorganic chlorides (e.g. NaCl) can be significant chlorine sources for PCDD/F formation¹². However, it is not understood or documented how NaCl participates in dioxin formation reactions and under what conditions NaCl behaves like, or not like, PVC plastic. This paper analyzes the thermodynamics of high temperature salt chemistry and the relationships between Cl₂, HCl and NaCl(g) and NaCl(c), where (g) indicates gas phase and (c) the condensed phase. The thermodynamic calculations were based on the data of Barin *et al.*¹³.

Formation of HCl: While organic chlorine can be readily converted to HCl during combustion, salt in hog fuel may be evaporated at high temperatures: NaCl(c) → NaCl(g). The equilibrium partial pressure for salt at 925°C is about 3000 ppm, which would be high enough to allow complete evaporation of all of the salt contained in a typical hog fuel to NaCl(g) in the furnace.

If any substance present in the boiler can take Na away from NaCl, then HCl would be formed. The chloride in the salt can be converted quantitatively by sulphur, if present, to HCl over the entire range of flue gas temperatures, as shown in Figure 1, according to the following reaction:



The sulphur content is usually very low in wood waste. However, Equation (1) could become important if high sulfur sludge is incinerated or if kraft pulping non-condensable gases (NCGs) or fuel oil, coal, or tire derived fuel (TDF), all containing sulphur, are co-fired in the boiler.

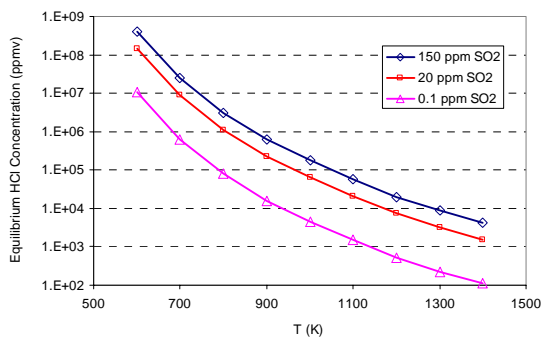


Figure 1. Equilibrium gas phase concentrations calculated for reaction (1) at 20% H₂O and 10% O₂.

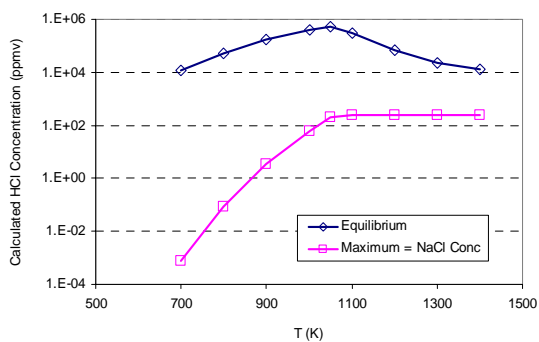
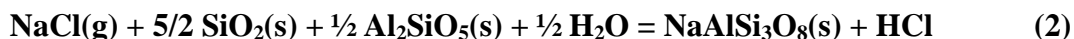


Figure 2. Equilibrium concentrations for reaction (2). assuming 0.47% NaCl in hog; 20% H₂O and 10% O₂ in flue gas.

Ash, usually rich in aluminum and silicon species, is found in significant quantities in hog fuel. NaCl reacts with alumina-silicates in the presence of water vapor, forming HCl. For example:



Reaction (2) has been studied extensively¹⁴ and the HCl equilibrium concentration for 0.47% NaCl in the hog fuel fired in Boiler E is illustrated in Figure 2 as an example. Due to relatively low mobility, the reaction with solid NaCl is not considered. The maximum HCl concentration at higher temperatures should be equivalent to the NaCl concentration.

Yasuhara *et al.*¹² reported that HCl emissions from incineration of newspaper were 23 and 640 mg/m³ at 12% O₂, respectively, with the addition of NaCl (3.1% Cl) and PVC (5.1% Cl). Such a dramatic difference must be attributed to the fact that the newspaper is a “clean” waste with little sulphur and inorganic ash and, therefore, little NaCl can be converted to HCl by reactions (1) and (2). In contrast, the chlorine contained in PVC should be converted primarily to HCl during combustion. These results are, therefore, consistent with the above analysis.

Our experimental results indicate that reactions (1) and (2) are not only thermodynamically favored but actually occurred in power boilers burning salt-laden hog fuel. Figure 3 shows the molar ratio of sodium to chloride in the process discharges from Boiler A. The solid fuel blend consisted of hog and sludge for all 5 tests, with a low sulphur coal added for the tests on 04/30/02 and 05/02/02. The fuel contained slightly more sodium than chloride with the Na/Cl molar ratio ranging from 1.4 to 2.3. The Cl content in the grate ash was lower than that in the fuel, at 0.02–0.11%, while the Na content was 4 to 20 times higher than that in the fuel, at 2.4–4.4%. As a result, the molar ratio of Na/Cl in the grate ash ranged from 14 to 196. These results indicate that not all the hog salt was evaporated, but that a significant portion of the salt was converted to HCl by reactions (1) and (2), with the Na being left with the grate ash. The conversion reactions not only occurred on the grate ash but also continued in the boiler and downstream flue gas, as indicated by the higher Na/Cl molar ratios than those in the fuel in both the air heater and multi-cyclone (MC) ash (2.0–5.2). The Na/Cl molar ratios were much lower in the scrubber effluent (0.33–0.83), reflecting the absorption of high concentrations of HCl in the scrubber.

In the presence of significant quantities of sulphur, reaction (1) should be the predominant reaction for salt conversion to HCl. For example, sample air heater deposits taken from Boiler C contained 10.3% Na, 1.5% Cl, and 22.6%

SO₄ on a weight basis. That is equivalent to a Na/Cl molar ratio of 10.3 and a Na₂/SO₄ molar ratio of 0.95. It is clear that with such low chloride content, sodium in the deposit is almost completely present as Na₂SO₄.

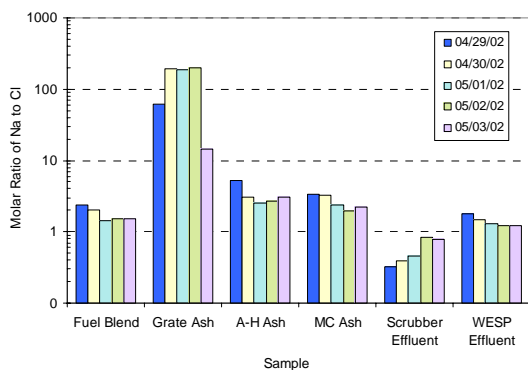


Figure 3. Distribution of Na and Cl in the fuel and in different ash streams for Boiler A.

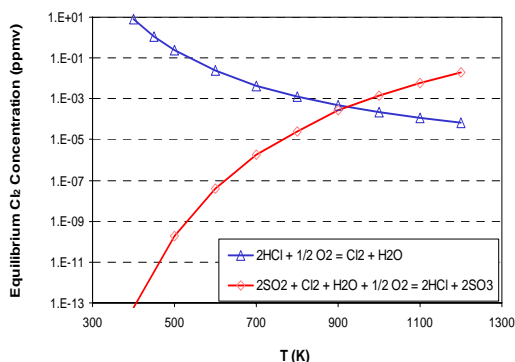


Figure 4. Equilibrium Cl₂ concentration calculated for reactions (3) and (4) at 20% H₂O, 10% O₂, with 20 ppm HCl, and with equal SO₂ and SO₃.

Formation and Reduction of Cl₂: Elemental chlorine is a highly reactive chlorinating agent for organic compounds. Cl₂ may be formed by oxidation of HCl according to the Deacon reaction:



The equilibrium Cl₂ concentration is four or five orders of magnitude higher at lower temperatures than at higher temperatures for a given HCl concentration, as shown in Figure 4. In the presence of O₂ and H₂O, however, Cl₂ may be reduced by oxidation of SO₂ according to



As shown in Figure 4, the thermodynamics of reaction (4) are also highly favored at lower temperatures (<600°C). The actual Cl₂ concentration should be determined by the relative kinetics of reactions (3) and (4). The rate of the Deacon reaction depends on the catalysts present in the process. Copper was reported in the literature as the most effective catalyst. Reaction (3) is thought to be slow in hog fuel boilers where the copper content is usually much lower than that in municipal solid waste incinerators. It is, therefore, expected that the Cl₂ concentration would be low when the flue gas sulphur content is high.

It is known that addition of sulphur can inhibit dioxin formation. However, the Cl/S ratio required has varied in the literature. Griffin¹⁵ reported a practical Cl/S ratio of as low as 0.1. The above thermodynamic analysis, i.e. reactions (1–4), indicates that sulphur converts NaCl to HCl and therefore increases the Cl₂ concentration. However, if the sulphur content is sufficiently high that there is still SO₂ left after consuming all the NaCl, then the excess SO₂ would reduce Cl₂ by reaction (4). Theoretically, as indicated by reaction (1), the molar ratio of Cl/S should be lower than 2, in order to completely convert NaCl to HCl and still have excess SO₂ for Cl₂ reduction. Our studies on power boilers burning salt-laden hog fuel indicate that a Cl/S ratio as high as 1 can significantly attenuate dioxins formation and emissions¹⁶.

Kinetic Modeling

In an attempt to identify means to reduce dioxin formation and emissions from power boilers burning salt-laden hog fuel, a semi-empirical kinetic model was developed. Several assumptions were made in the model development: 1) Fuel PCDDs/Fs, if any, are destroyed in the furnace at high temperatures. 2) Dioxin precursors (PRECs) are formed in combustion from Cl and fuel organic compounds. 3) PAHs are formed in combustion processes and carried over in the downstream flue gas. 4) PCDDs/Fs are formed in the downstream processes via the precursor (5) and *de novo* (6) reactions and the reverse and PCDD/F destruction reactions are not considered:



where M represents active catalysts (solid). Cl represents NaCl(g), HCl, Cl₂ and/or Cl•. It is likely that the most reactive Cl species are Cl• for formation of precursors and Cl₂ for the *de novo* reaction. 5) The reactions are assumed to be first order relative to the reactants in the above reactions.

Stack Emission Model: If the Toxic Equivalent (TEQ) concentration is used to represent the total PCDD/Fs, the TEQ formation rate in the downstream flue gas may be expressed as

$$d[\text{TEQ}]/dt = k_5[\text{PREC}] + k_6[\text{PAH}][\text{Cl}_2] \quad (7)$$

It is assumed in the above expression that both O₂ and ash catalyst (M) contents are in great excess.

Once formed in the flue gas, the PCDD/Fs would either be removed together with fly ash or emitted from the stack. How much is emitted depends not only on the amount formed but also on the removal efficiency. It is thus possible that a boiler with less (or more) formation of PCDD/Fs has higher (or lower) TEQ emissions because of different boiler design characteristics and operating conditions (e.g. different particulate removal efficiencies). A kinetic model for stack TEQ emissions may be developed, starting from the following equation:

$$[\text{TEQ}]_{\text{stack}} = X \cdot \{[\text{TEQ}]_{\text{non}} + [\text{TEQ}]_{\text{de novo}}\} \quad (8)$$

where X represents the fraction of formed PCDD/Fs escaping to the stack. The fraction being removed with ash in the ESP is, therefore, (1-X). The subscripts “*de novo*” and “non” indicate formation, respectively, by *de novo* synthesis and by non-*de novo* mechanisms or from precursors.

For a first approximation, $[\text{TEQ}]_{\text{non}}$ is simply assumed to be a constant in the development of this model. As this term is related to combustion performance, such an approximation should be valid for good combustion conditions, as observed in the majority of our stack tests. The concentration of Cl_2 in the flue gas is not known. For simplicity, it is assumed to be determined by the equilibrium of the Deacon reaction, i.e. equation (3), in the absence of excess SO_2 :

$$[\text{Cl}_2] = \frac{[\text{HCl}]^2 [\text{O}_2]^{1/2}}{[\text{H}_2\text{O}]} \exp(-\Delta G^\circ_3 / RT) \quad (9)$$

where R is the gas constant and T is the reaction temperature in °K. ΔG°_3 is the free energy change of reaction (3) at the standard state. There are two dioxin emission vectors: gas phase (subscript g) and particulate phase (p) emissions. By definition,

$$X = \frac{[\text{TEQ}_p]_{\text{stack}} + [\text{TEQ}_g]_{\text{stack}}}{[\text{TEQ}]_{\text{ESP}} + [\text{TEQ}]_{\text{stack}}} \approx \frac{[\text{TEQ}_p]_{\text{stack}}}{[\text{TEQ}]_{\text{ESP}}} + \frac{[\text{TEQ}_g]_{\text{stack}}}{[\text{TEQ}]_{\text{ESP}}} \quad (10)$$

The approximation made in the above equation is based on the fact that over 90% of the total TEQ is typically removed in the ESP of the power boilers burning salt-laden hog fuel¹. The first term on the right side is related to the ESP efficiency and second term is a function of the ESP temperature under equilibrium conditions.

It is further assumed that the HCl concentration is proportional to the hog salt content. After a series of substitutions and simplifying treatments, the integrated Equation (7) gives Equation (11):

$$[\text{TEQ}]_{\text{stack}} = A + B \cdot \exp(-C/T_{\text{ESP}}) + D \cdot [\text{PAH}]_{\text{stack}} \cdot [\text{NaCl}]_{\text{hog}}^2 \quad (11)$$

where A, B, C and D are model parameters to be estimated with experimental data. The first term on the right hand side reflects the particulate phase dioxin emissions and is determined by the ESP efficiency. The second term represents the gas phase emissions and is a function of the ESP temperature. The third term is related to *de novo* synthesis.

Model Validation, Data Correlation and Discussion: Only the high molecular weight (HMW) PAH species (those with ≥ 4 rings) are included in calculating $[\text{PAH}]_{\text{stack}}$ in Equation (11). The correlation of 15 test results from Mill F with Equation (11) is shown in Figure 5. The data scatter is apparent. However, given the nature and reproducibility of stack tests on full-scale power boilers with operating conditions frequently “uncontrollable” and all the simplifications made in model development, the correlation should be accepted as being fairly good.

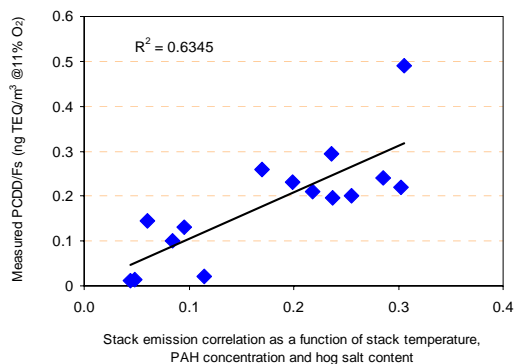


Figure 5. Validation of stack dioxin emission model with test data from Mill F.

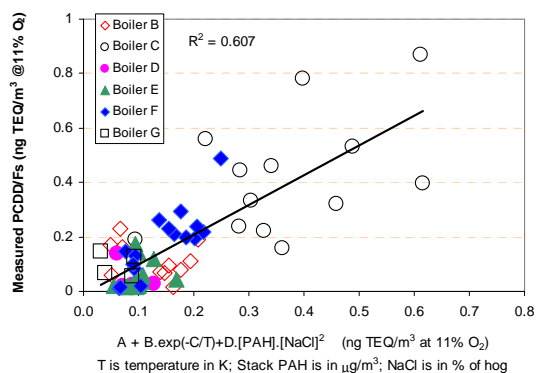


Figure 6. Intermill data correlation based on single stack tests.

The stack emission model was further verified with 62 test results obtained on all of the 6 power boilers with a dry ESP. Results from the two boilers with wet scrubbers, Boilers A and H, are not included in the verification database. Good agreement between the experimental data and the model is illustrated in Figure 6. While the good fit between the measured emissions and the correlation is evident, fitted values of the parameters A, B, and D do not offer much significance because of the arbitrary units used in the correlation. However, the value of C, 5650, suggests that the free energy change for desorption of PCDD/Fs from the ash particles is about 47 kJ/mol at ESP temperatures. The magnitude of this figure seems to be reasonable, and compares favorably with the range of 45 to 53 kJ/mol provided by Altwicker *et al.*¹⁷ for the PCDD/F solid-to-gas desorption step.

Summary

This paper presents a thermodynamic analysis of high temperature salt chemistry and its influence on PCDD/F formation in power boilers burning salt-laden wood waste. A semi-empirical kinetic model has also been developed to predict stack dioxin emissions from these boilers. The following conclusions were drawn:

Hog salt can evaporate completely during combustion to form gaseous NaCl. HCl and Cl₂ are not products of combustion of salt-laden wood waste but form by converting NaCl through reactions with SO₂ or alumina-silicate materials. HCl can be catalytically oxidized by O₂ to Cl₂. The presence of sulphur at low concentrations (Cl/S>2) enhances PCDD/F formation by increasing HCl and Cl₂ concentrations. The presence of sulphur at high concentrations inhibits *de novo* formation of PCDD/Fs through Cl₂ reduction by excess SO₂. The kinetic model considers both precursor and *de novo* formation mechanisms and also incorporates the results of our thermodynamic analysis. The model has been verified with both intra-mill and inter-mill test data. Stack dioxin emissions increase linearly as the ESP efficiency decreases, exponentially with increasing ESP temperature, and to the second order with hog salt content.

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