

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

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ABSTRACT

It has been demonstrated that both organic chlorine (e.g. PVC) and inorganic chlorides (e.g. NaCl) can be significant chlorine sources for PCDD/F formation during combustion processes. However, it is not precisely known how NaCl participates in dioxin formation reactions and under what conditions NaCl behaves like, or unlike, PVC. This paper presents a thermodynamic analysis of high temperature salt chemistry. Its influence on dioxin and furan formation in power boilers burning salt-laden wood waste is examined through the relationships between Cl_2 , HCl, NaCl (g) and NaCl (c). Our thermodynamic analyses indicate that HCl and Cl_2 are not products of combustion of salt-laden wood waste but are formed when sulfur is burned with even ash-free hog fuel. HCl is a product of combustion of PVC-laden municipal solid waste. NaCl can be converted to HCl by reactions with SO_2 or alumina-silicate materials. HCl can be oxidized to Cl_2 by O_2 , and Cl_2 can be reduced back to HCl by SO_2 . The presence of sulfur at low concentrations thus enhances PCDD/F formation by increasing HCl concentrations. At high concentrations, sulfur inhibits de novo formation of PCDD/Fs through Cl_2 reduction by excess SO_2 . NH_3 can similarly reduce Cl_2 to HCl, and therefore, may inhibit de novo formation of PCDD/Fs. Nitrogen oxide, NO, does not have any effect on dioxin and furan formation. The effect of carbon monoxide, CO, on dioxin and furan formation cannot be determined by thermodynamic analyses alone.

A semi-empirical kinetic model is proposed, describing the PCDD/F formation rate in power boilers burning salt-laden wood waste. This kinetic model considers both precursor and de novo formation mechanisms. A simplified version is used as a stack emission model. The kinetic model indicates that stack dioxin emissions will increase linearly with decreasing electrostatic precipitator (ESP) efficiency, exponentially with increasing ESP temperature, and to the second order with hog salt content. The stack emission model was verified with both intra-mill and inter-mill test data. Stack dioxin emissions were also found to increase exponentially with the air heater inlet temperature. Both mill-averaged test results and those obtained in two pilot-scale combustors support this correlation.

INTRODUCTION

Burning salt-laden wood waste in power boilers can lead to the formation and emission of dioxins and furans under certain combustion conditions [1, 2]. For the last few years, coastal mill operators in British Columbia have been collaborating on a research and testing program with the Pulp and Paper Research Institute of Canada and the University of British Columbia to quantify the emission levels and understand the main formation mechanisms of dioxins/furans in their facilities, and to identify and evaluate possible measures or approaches that will reduce, minimize or prevent emissions. Experimental results from this program are presented and discussed separately [3-8].

Analysis of stack test data indicated that the formation mechanisms proposed in the literature for solid waste incinerators, namely precursor and de novo, may also be applied to the power boilers burning salt-laden hog fuel. Poor combustion conditions in the furnace favor the formation of gas-phase precursors, such as chlorophenols and PAHs, leading to dioxin/furan formation through condensation and adsorption/desorption reactions on ash particles [4]. Also, high flue gas temperatures in the heat exchanging and gas cleaning zones favor dioxin/furan formation through solid-phase reactions on fly ash involving certain catalysts and unburnt carbon [5]. A combination of the two mechanisms may be encountered in a given boiler [5], depending on its design and operational parameters. These findings are consistent with many of the literature results. For example, Kilgroe [9] and Everaert and Baeyens [10] reported that improving combustion conditions in the furnace and lowering ESP temperatures significantly lowered dioxin/furan emissions.

Efforts have been made by several research groups to develop thermodynamic and kinetic models describing dioxin formation and predicting experimental results obtained on various facilities of different scales. Tan et al. [11] presented a comprehensive thermodynamic model, consisting of hundreds of C/H/O/N/Cl species, based on three computer databases. Modeling results indicated that the PCDDs and PCDFs measured in an industrial iron ore sinter plant were not in equilibrium with each other. Dioxins and furans cannot exist thermodynamically in any significant quantities in oxidizing combustion processes and may become stable only at oxygen concentrations below 10^{-35} bar ($T = 600-800$ K). Thus, the thermodynamics determine that PCDD/Fs can only be formed at localized sites as intermediate products with trace concentrations. The intermediate products may become "permanent" if the reaction conditions kinetically inhibit their subsequent, complete oxidation.

Given the general complexity of thermodynamic models, it is difficult to use them to interpret the overall process of dioxin formation. Also, the model developed by Tan et al. [11] did not include solid phase and chloride species.

Studies on whether the total chlorine level was important for the formation of PCDD/Fs have led to contradictory conclusions. For instance, Yasuhara et al. [12] studied the role of inorganic chlorides on the formation of PCDD/Fs in incineration processes. They found that dioxin formation increased with the NaCl content in impregnated newspapers being incinerated. Wikstrom et al. [13] investigated PCDD/F formation in the combustion of an artificial fuel, containing 34% paper, 30% wheat floor, 14% sawdust, plastic materials, and metals, with PVC or CaCl_2 added. No correlation was found between the levels of dioxin formation and the fuel

chlorine content. Our own results [3-5] obtained on eight hog fuel power boilers at BC coastal pulp mills showed little correlation between dioxin emissions and hog salt levels, except for one mill (Mill F) [6] for which dioxin emissions increased with increasing hog salt content. Furthermore, Mills D, E, and H, the three mills with the lowest dioxin emissions, burned hog fuels with the highest salt contents [3, 5]. The salt content of the hog fuel burnt in the UBC pilot plant combustor was even higher (up to 2.5%) [7]. However, the levels of PCDD/F contained in the baghouse ash during the pilot plant tests were generally very low.

Chlorine may be present in different forms in a combustion process and gas-phase and solid-phase chlorine speciation may affect the formation of PCDD/Fs. Wikstrom et al. [14] reported that while ash bound chlorine alone was a sufficient chlorine source for *de novo* formation, the addition of HCl to the system did not influence the yields of the PCDD/Fs, nor the degree of chlorination. The results of this and other work [15, 16], therefore, showed that HCl is a weak chlorinating agent. Although HCl can readily react with oxidizing radicals, such as OH• and HO₂•, in combustion to produce Cl•, it would be much more difficult to dissociate HCl into H• and Cl• radicals than Cl₂ into Cl• radicals. This is due to a much stronger H-Cl bond (430 kJ/mole) than Cl-Cl bond (240 kJ/mole) [14]. Given that Cl• is a very reactive radical, it can be concluded that Cl₂ will be a strong chlorinating agent. It was observed [14] that the yields of PCDD/Fs in the presence of only Cl₂ were similar to those with both Cl₂ and Cl• present. However, the concentration of HCl in incineration processes is much higher than that of Cl₂. In addition, Addink et al. [17] have observed that the *de novo* formation rate in the presence of high concentrations of HCl is similar to that in the presence of high concentrations of Cl₂.

In power boilers burning salt-laden hog fuel, the chlorine is introduced mainly as NaCl. Addink et al. [18] found that NaCl could be a chlorinating reagent for formation of PCDFs on aqueous extracted incinerator fly ash. However, PCDDs were not formed, possibly because the PCDD formation catalyst had been removed through the extraction process. No difference was made by adding NaCl to the as-received incinerator ash, suggesting that NaCl was not as reactive as other chlorine sources originally present in the ash.

To our knowledge, high temperature salt chemistry and its influence on dioxin formation in combustion and thermal processes have not been thoroughly studied. Being of particular interest to the operators of power boilers burning salt-laden hog fuel, a thermodynamic analysis of the salt chemistry will be provided in this paper.

Most of the kinetic models available in the literature to describe PCDD/F formation rates are empirical. Mätzing [19] proposed a kinetic model for *de novo* synthesis assuming the fly ash carbon oxidation reaction was first order in carbon and a half order in oxygen, leading to CO_x, PCDDs, and PCDFs. The fraction of the carbon being oxidized to PCDD/Fs was assumed to depend on the amount of catalyst present. It also considered further oxidation of the formed PCDD/Fs on fly ash surfaces. This model contained 6 reaction rate constants, and required 2 parameters, i.e. the pre-exponential factor and the activation energy, to be estimated for each rate constant. The kinetic model derived by Huang and Buekens [20] for *de novo* synthesis of PCDD/Fs was based on similar mechanistic steps as those in Mätzing's model [19], i.e. carbon gasification with O₂, PCDD/F formation, desorption, and degradation. This model contained a total of 8 unknown parameters. Altwicker *et al.* [21] developed an empirical model based on a

four-step dioxin precursor formation mechanism: solid and gas phase precursor reactions to form solid phase dioxins; desorption of solid phase dioxins into the gas phase; solid phase dioxin dechlorination, and solid phase dioxin decomposition. This model contained 4 reaction rate constants, each with two parameters to be estimated. While the most active temperature range for *de novo* formation of PCDD/Fs is known to be 300-350° C, this model showed a maximum rate for the formation of PCDDs from precursors at 250-300° C. Altwicker *et al.* [22] further compared the relative rates of precursor and *de novo* formation and concluded that the precursor reactions tended to be much faster and could occur in a wider temperature range (up to 600° C) than those associated with the *de novo* mechanism.

It is clear that a comprehensive model should include both precursor reactions and *de novo* synthesis. Stanmore [23] extended an empirical model for *de novo* formation on fly ash to include the precursor mechanism and a gas phase formation component. This model employed a sticking factor quantifying the adsorption potential of gaseous reactants (e.g. HCl, Cl₂ and/or precursors) on the ash surface. The value of the sticking factor was found to decrease exponentially with increasing sulfur concentrations in the flue gas. Since the dioxin formation rate increases linearly with an increasing sticking factor value, the model predicts that sulfur would inhibit dioxin formation. The sulfur effect was also studied by Mueller *et al.* [24] using a large computer model. It consisted of 199 elementary reactions to describe the C/H/O/N system, 36 more reactions involving Cl, and up to 91 additional reactions to cover sulfur interactions with O and N species. Unfortunately, this model only deals with radical chain reactions occurring at high temperatures (e.g. >800° C) in combustion and post-combustion gases. As will be seen later, oxidation of SO₂ and HCl are not thermodynamically favored at high temperatures and, therefore, this detailed model has only limited use in explaining and predicting the effect of sulfur and chlorine on PCDD/F formation, which occurs mainly at lower temperatures.

Even the above empirical models are complicated, containing 8 – 12 parameters which need to be estimated. It would be very difficult to apply any of these models to describe dioxin formation and emissions from full-scale power boilers or incinerators. After an analysis of the test results and operating parameters on 12 municipal solid waste incinerators, Everaert and Baeyens [10] obtained 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 BC coastal power boilers burning salt-laden hog fuel [3], the effect of ESP temperature given in the correlation agrees qualitatively with the measured emission data for power boilers burning salt-laden hog fuel [5]. In this work, we will attempt to develop a semi-empirical model based upon both thermodynamic analysis and kinetic considerations.

EXPERIMENTAL

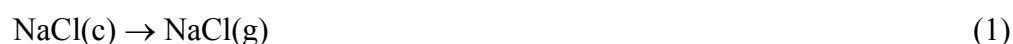
The main experimental results on which our kinetic model is developed and verified are presented elsewhere [3-5]. These experiments were conducted on 8 full-scale power boilers burning salt-laden hog fuel, operated by BC coastal pulp mills. The general design information and specifications for these boilers are given separately [3, 5]. The same letter designation (A through H) used in the other papers [3-5] is also assigned to label the various mills and their power boilers in this paper.

THERMODYNAMIC ANALYSIS

It has been demonstrated that both organic chlorine (e.g. PVC) and inorganic chlorides (e.g. NaCl) can be significant chlorine sources for PCDD/F formation [25]. 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 section analyzes the thermodynamics of high temperature salt chemistry and the relationships between Cl₂, HCl and NaCl(g) and NaCl(c), where (g) indicates NaCl in the gas phase and (c) in the condensed phase. The thermodynamic calculations were based on the thermo-chemical data of Barin et al. [26].

Formation of HCl

While organic chlorine can be readily converted to HCl during combustion, salt in hog fuel may be evaporated at high temperatures according to



The equilibrium partial pressure for salt at 925° C is about 3000 ppmv, which would be equivalent to 6.5% salt by weight in the fuel for a hog fuel boiler. Since the actual NaCl content in the fuel fed to these hog fuel boilers is well below 6.5%, it may be possible in the absence of other reactions that the fuel NaCl be completely vaporized in the furnace and present as NaCl(g).

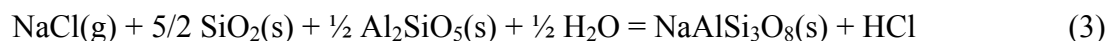
If any substances can take Na away from NaCl, then HCl would be formed. For example, the chloride in the salt would be converted quantitatively by sulfur, if present, to HCl over the entire range of flue gas temperatures, as shown in Figure 1, according to the following reaction:



The HCl concentration resulting from this reaction may be calculated from the sulfur input to the combustion system.

The sulfur content is usually very low in wood waste but may be significant in sludge. Therefore, the contribution from Equation (2) would be limited in power boilers burning “clean” hog fuel. However, Equation (2) could become important if sludge is burnt in significant quantities and the sulfur content in sludge is high (e.g. for Mill H), or if non-condensable gases (NCGs) or fuel oil, coal, or tire derived fuel (TDF), all containing sulfur, are co-fired.

Ash, usually rich in aluminum and silicon species, is found in significant quantities in solid fuels like hog fuel. NaCl reacts with alumina-silicate in the presence of water vapor, forming HCl. An example of a group of such reactions is given as follows:



Reaction (3) has been studied extensively [27] 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 a relatively low mobility of reactants in the condensed phases, the reaction with gaseous NaCl should be predominant and the reaction with solid NaCl is not considered. The maximum HCl

concentration at higher temperatures should be then equivalent to the NaCl concentration in the combustion system.

Yasuhara et al. [25] reported that HCl emissions from incineration of newspaper were 23 and 640 mg/m³ @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 sulfur and inorganic ash and, therefore, little NaCl can be converted to HCl by reactions (2) and (3). 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 own experimental results indicate that reactions (1-3) are not only thermodynamically possible but actually occur 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 sulfur 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, indicating the contribution of Na from non-chloride ash and sludge in addition to hog salt. The chloride content in the grate ash was lower than that in the fuel, at 0.02-0.11%, while the sodium 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, as shown in Figure 3. These results indicate that not all the hog salt was evaporated according to reaction (1), but that a significant portion of the salt was converted to HCl by reactions (2) and (3), with the sodium 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). However, the Na/Cl molar ratio became much lower in the scrubber effluent (0.33-0.83), reflecting the absorption of high concentrations of HCl in the scrubber. Since the Na/Cl molar ratio measured in the wet ESP effluent (1.2-1.8) was close to the ratio in the fuel, it may be concluded that the flue gas in the wet ESP contained much more salt particulate than HCl. This is further confirmed by the stack test results which showed very low HCl emissions (0.3-9 mg/m³) and relatively high particulate emissions (42-176 mg/m³).

In the presence of significant quantities of sulfur, reaction (2) 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. It is not certain, however, whether Na₂SO₄ was formed in the flue gas and then deposited on the air heater surface or NaCl deposited first and then reacted with SO₂ present in the flue gas to form Na₂SO₄ on the surface.

In summary, the salt vapor concentration in the flue gas depends very much on the hog salt content, but the HCl concentration may not be determined by the salt content. Instead, the HCl concentration is mainly controlled by the sulfur concentration and, to a lesser degree, by the quantities and properties (e.g. surface area) of alumina-silicate matters.

Reduction of Cl₂ by Sulfur

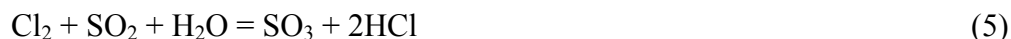
Once formed at high temperatures, HCl will be present throughout the boiler. Although metal oxides, such as CaO, MnO, ZnO, are present in the ash, the consumption of HCl through chlorination of these species occurs only at lower temperatures (e.g. 400°C) where gas-solid reactions are relatively slow. Therefore, significant removal of HCl is not likely in entrained flow with a short residence time (on the order of seconds) in the downstream flue gas, unless major quantities of acid gas adsorbents (e.g. lime) are added.

Elemental chlorine may be formed by oxidation of HCl according to reaction (4):



This is a gas phase reaction at high temperatures, leading to a low equilibrium Cl₂ concentration, as illustrated in Figure 4. At low temperatures, however, it is known as the Deacon process, a heterogeneous catalytic 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.

In the presence of SO₂, however, Cl₂ may be reduced by oxidation of SO₂ according to reaction (5):



The above reaction is thermodynamically very much favored. SO₂ may also be oxidized by O₂:



Since O₂ is present in great excess in combustion processes, reaction (6) should be considered to be competing with reaction (5) for SO₂. As shown in Figure 5, the thermodynamics of the combined reactions (5) and (6) remain highly favored at temperatures below 600° C. The actual Cl₂ concentration depends on the relative kinetics of reactions (5) and (4). The rate of the heterogeneous reaction (4) depends on the levels of effective catalysts present in the process. Copper was reported in the literature as the most effective catalyst for the Deacon reaction. This reaction is thought to be slow in hog fuel boilers where the copper content is usually very low, much lower than that in municipal solid waste incinerators. It is, therefore, expected that the Cl₂ concentration would be low when the fuel, or flue gas, sulfur content is high.

In summary, sulfur converts NaCl by reaction (2) and hence increases the HCl concentration in the flue gas. However, if the sulfur content is sufficiently high that there is still SO₂ left after consuming all the NaCl, then the excess SO₂ would reduce Cl₂ by reaction (5). As indicated by reaction (2), the molar ratio of Cl/S should be lower than 2, in order to completely convert NaCl to HCl.

It has been generally accepted that addition of sulfur can inhibit dioxin formation through reaction (5). However, the Cl/S ratio required for a substantial effect has varied from 0.1 to 1.2 [28-30]. An interpretation of reasons for these variations is not available in the literature and a

summary of our understanding, based on the above thermodynamic analysis, i.e. reactions (1-6), is therefore presented below.

In theory, the concentration of excess SO_2 does not have to be very high to completely reduce Cl_2 , since the Cl_2 concentration is low in the combustion process, compared to the total amount of chlorine present in the fuel. Therefore, the theoretical maximum molar ratio of Cl/S for the sulfur effect, or “theoretical Cl/S ratio”, can be actually quite high (≥ 2) and variable, depending on the original chlorine source and ash behavior. The theoretical Cl/S ratio should be close to 2, as mentioned above, if the fuel chlorine source is salt. If the fuel chlorine source is organic, such as PVC, then reaction (2) would become insignificant and all the sulfur present in the flue gas should be available for Cl_2 reduction by reaction (5). In such a case, the maximum theoretical Cl/S ratio could still be much greater than 2 without affecting the ability for the sulfur to inhibit dioxin formation.

In practice, however, sufficiently high SO_2 concentrations are necessary to maintain a reasonable rate for reaction (5). Therefore, the practical Cl/S ratio is likely to be much smaller than the theoretical ratio. A practical Cl/S ratio of as low as 0.1, as reported by Griffin [28], may be excessive and a value of 1 to 2 should be adequate, which is consistent with previous observations [29, 30]. A “memory” effect was observed in sulfur addition trials [29, 30] and the above practical Cl/S ratio is applicable only after the memory effect has been eliminated. The present study also proposes that the “memory” effect associated with the sulfur effect is caused, at least partially, by reaction (2). The injected sulfur must first consume all the metal chlorides (e.g. NaCl, KCl, and CaCl_2) accumulated on the equipment surfaces, in addition to the salt introduced continuously with the fuel, before becoming available for reaction (5). The memory effect very much depends on the total amount of accumulated metal chlorides, as well as the thickness of the deposits. Generally, the higher the excess SO_2 , the shorter should such a “memory” be.

It was shown in a separate paper [3] that PCDD/F emissions were reduced for Boiler C when SO_2 and HCl emissions were both high. In that case, the effect of SO_2 may be attributed to reaction (5), while the effect of HCl is not clear. The high HCl emissions were primarily a result of NaCl conversion at high SO_2 concentrations, according to reaction (2), with the contribution from reaction (5) being secondary.

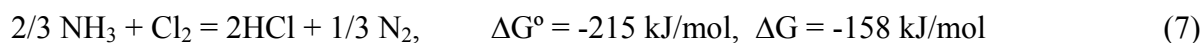
Sulfur injection may be considered as an option for dioxin control. Its impact on the formation of corrosive species, such as HCl, Cl_2 , and SO_3 [8], on equipment corrosion [8] and on boiler plugging propensity [30] was discussed in detail by earlier papers in this series [3-5].

Effect of NH_3 , CO, and NO_x

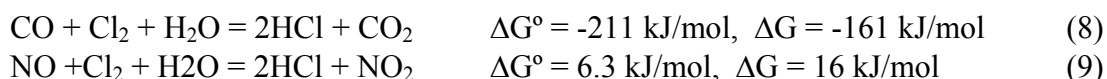
Experimental studies [31-33], including pilot plant studies on salt-laden wood combustion at CANMET and full scale trials at Mill D, have indicated that ammonia, urea, and other nitrogen-containing compounds may also reduce PCDD/F formation. Little is known about the mechanism for the effect. Some authors [32, 33] speculated that certain nitrogen-containing species might form stable inactive transition metal complexes so that metallic catalytic sites would be deactivated. However, our thermodynamic analyses indicate that it is not possible to form stable metal-ammonia complexes under oxidizing flue gas conditions in the de novo

temperature range (e.g. 250-500° C). We, therefore, conclude that the effect of ammonia cannot be explained by catalyst deactivation. Although alkali and alkali-earth metal compounds like CaO, Ca(OH)₂, and Na₂CO₃, are used in many processes to adsorb and remove HCl from combustion flue gases, NH₄Cl(s) cannot be formed under flue gas conditions at temperatures above 170° C. Thus, the effect of ammonia cannot be explained by HCl removal, either.

We propose that like sulfur species, ammonia and other nitrogen containing compounds inhibit PCDD/F formation by reducing elemental chlorine to hydrogen chloride. For example, for a flue gas composition of 20% H₂O, 10% CO₂, 5% O₂, 100 ppm HCl, 10 ppm NH₃, 1 ppb Cl₂, and balance N₂ at 700 K,



where ΔG° and ΔG denote the chemical free energy change of the reaction at the standard state and under the specified conditions, respectively. Since $\Delta G \ll 0$ for reaction (7), thermodynamically 10 ppm of NH₃ can reduce Cl₂ to much lower than 1 ppb. Kinetically, reaction (7) is expected to go through fast radical chain reactions, like the thermal DeNO_xTM process with NH₃ [31]. It is relatively easy to dissociate Cl₂ [14] and, therefore, reaction (7) should occur at lower temperatures than the thermal DeNO_xTM process. The effect of other nitrogen-containing compounds can be readily explained in the same way. Similar thermodynamic analysis was conducted for CO and NO_x at 1000 ppm CO, 100 ppm NO, 10 ppm NO₂, and otherwise the same composition as given above.



Since $\Delta G > 0$ for reaction (9), NO does not have the potential to reduce Cl₂ and should not affect dioxin formation. Reaction (8) indicates that CO has a high potential to reduce Cl₂ and hence can inhibit de novo formation of PCDD/Fs. However, CO is a product of incomplete combustion and a high concentration of CO is usually an indicator of high concentrations of dioxin precursors. The effect of CO is therefore complicated, depending on the kinetics of the de novo and precursor reactions. This complication may explain poor correlations between PCDD/F emissions and CO emissions, as observed in our tests [4] and reported in the literature [34].

KINETIC MODELING

Basic Assumptions

The following assumptions were made in the model development:

- 1). PCDDs/Fs contained in the fuel are destroyed completely in the furnace at high temperatures so that all the dioxins and furans are formed downstream in the flue gas at lower temperatures.
- 2). Dioxin precursors are formed in combustion from chlorine and fuel organic compounds (OCs). Since we did not measure or test for these precursors in the present study, they are not identified or distinguished in the model. The total amount of precursors is referred to as PRECs.



3. PAHs are also formed in combustion processes and are not destroyed in the downstream flue gas. As PAHs were measured in most of the stack dioxin tests covered by the present study, it is assumed that the total amount of PRECs formed is positively correlated to the total amount of PAHs.



4. PCDDs/Fs are formed in flue gas in the generating bank, economizer, air heater, multi-cyclones, and ESP via the following precursor (12) and de novo (13) reactions:



The majority of the literature supports the theory that precursor reactions lead primarily to PCDDs and de novo reactions to PCDFs [22]. For simplicity, however, this difference is not considered in the model development. M in the above reactions represents active catalysts (solid). Cl represents NaCl(g), HCl, Cl₂ and/or Cl•. It is likely that the most reactive chlorine species is in the form of Cl• for reaction (10) and Cl₂ for reaction (13).

5. The reaction takes place in an entrained plug flow reactor. Since the gas and solids residence times in the effective zone are short, and the levels of PCDDs/Fs formed are low, the reverse and PCDD/F destruction reactions are not considered here.

6. The reactions are assumed to be first order relative to the reactants in the above reactions.

Kinetic Expressions

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

$$d[\text{TEQ}]/dt = k_{12}[\text{PREC}] + k_{13}[\text{PAH}][\text{Cl}_2] \quad (14)$$

It is assumed in the above expression that both oxygen and ash catalyst (M) contents are in great excess. Both [PAH] and [PREC] are functions of combustion conditions and symbolically expressed as

$$[\text{PREC}] = f_{10}(T_c, t_c)[\text{Cl}\bullet] \quad (15)$$

$$[\text{PAH}] = f_{11}(T_c, t_c) \quad (16)$$

where T_c and t_c represent combustion temperature and time, respectively. Inserting equation (15) into equation (14) yields

$$d[\text{TEQ}]/dt = k_{12} f_{10}(T_c, t_c)[\text{Cl}\bullet] + k_{13}[\text{PAH}][\text{Cl}_2] \quad (17)$$

Stack Emission Model

Once formed in the flue gas, the PCDD/Fs would either be removed together with fly ash or emitted from the stack. The total TEQ formation rate may be determined by combining the ash and stack TEQ removal rates (e.g. in ng/h). 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) [1].

In the absence of added sorbents, such as activated carbon, PCDD/Fs removal is mainly by condensation and adsorption onto ash particles and then separation of the particles from the flue gas in the ESP or scrubber. A kinetic model for stack TEQ emissions may be developed from the following starting equation:

$$[\text{TEQ}]_{\text{stack}} = X \cdot \{[\text{TEQ}]_{\text{non}} + [\text{TEQ}]_{\text{de novo}}\} \quad (18)$$

where $[\text{TEQ}]$ represents the concentration of TEQ in flue gas (ng/m^3) and 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 subscript “de novo” indicates formation by *de novo* synthesis, and the subscript “non” indicates formation by non-*de novo* mechanisms or from precursors.

The sum of $[\text{TEQ}]_{\text{non}}$ and $[\text{TEQ}]_{\text{de novo}}$ gives the total formation and may be obtained by integrating equation (17). Since the reactions take place in the economizer and air heater (non-isothermal zones), integrating equation (17) requires knowing the relationship between the reaction time and temperature. For a first approximation, the first term on the right hand side of equation (18), $[\text{TEQ}]_{\text{non}}$, 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 the stack tests. For this reason, the results from tests with poor combustion conditions were excluded from the database for model verification.

The concentration of Cl_2 in the flue gas depends on the rates of reactions (4) and (5), which are not known. For simplicity, it is assumed that the concentration of Cl_2 is determined by the equilibrium of the Deacon reaction, i.e. equation (4), in the absence of excess SO_2 :

$$[\text{Cl}_2] = \frac{[\text{HCl}]^2 [\text{O}_2]^{1/2}}{[\text{H}_2\text{O}]} \exp(-\Delta G^{\circ}_4 / RT) \quad (19)$$

where R is the gas constant and T is the reaction temperature in $^{\circ}\text{K}$. ΔG°_4 is the free energy change of reaction (4) at the standard state. It varies with temperature and is estimated to be -18 and -11.4 kJ/mol at 600 and 700 $^{\circ}\text{K}$, respectively.

For a given stable operation, the oxygen and moisture contents do not change in the downstream flue gas. In the absence of significant quantities of an effective absorbent for HCl, the concentration of Cl_2 would only depend on temperature. Therefore, let

$$Q = \frac{[\text{HCl}]^2 [\text{O}_2]^{1/2}}{[\text{H}_2\text{O}]} \quad (20)$$

Then Q may be treated as a constant in the *de novo* reaction zone for a specific test. Express the rate constant of reaction (13) in an Arrhenius form:

$$k_{13} = A_{13} \cdot \exp(-E_{13}/RT) \quad (21)$$

where E_{13} represents the activation energy and both A_{13} and E_{13} are independent of temperature.

The concentration of PAHs is mainly determined by upstream combustion conditions and may be considered constant in the *de novo* zone.

$$[\text{TEQ}]_{\text{de_novo}} = A_{13} \cdot [\text{PAH}] \cdot Q \cdot \int \exp\left(-\frac{\Delta G^{\circ}_4 + E_{13}}{RT}\right) dt \quad (22)$$

The magnitude of E_{13} is not known. However, as $\Delta G^{\circ}_4 < 0$ and $E_{13} > 0$, the temperature dependency of the *de novo* reaction would be weakened by the combined activation energy of $\Delta G^{\circ}_4 + E_{13}$. The physical meaning is that the rate constant of reaction (13) increases with temperature but that the Cl_2 concentration decreases with increasing temperature, as illustrated in Figure 4. There must exist a weighted mean temperature, T_m , such that over the integration zone,

$$\int \exp\left(-\frac{\Delta G^{\circ}_4 + E_{13}}{RT}\right) dt = \exp\left(-\frac{\Delta G^{\circ}_4 + E_{13}}{RT_m}\right) \cdot \tau \quad (23)$$

where τ represents the residence time of flue gas in the space where the *de novo* reactions occur.

Let $k(T_m)$, a function of the mean temperature, be the apparent reaction rate constant

$$k(T_m) = A_{13} \exp\left(-\frac{\Delta G^{\circ}_4 + E_{13}}{RT_m}\right) \quad (24)$$

Then equation (22) may be simplified into

$$[\text{TEQ}]_{\text{de_novo}} = k(T_m) [\text{PAH}] \cdot Q \cdot \tau \quad (25)$$

Equation (18) is thus converted to

$$[\text{TEQ}]_{\text{stack}} = X \cdot [\text{TEQ}]_{\text{non}} + (X/V) \cdot K(T_m) \cdot \tau \cdot [\text{PAH}]_{\text{stack}} \cdot [\text{HCl}]^2 \quad (26)$$

where $K(T_m) = k(T_m) \cdot [O_2]^{1/2} / [H_2O]$, is again a function of the mean de novo reaction temperature, and V represents the fraction of the total amount of PAHs that escape the boiler and exit the stack. That is, $[PAH]_{stack} = V \cdot [PAH]$. There are two dioxin emission vectors: gas phase emission and particulate phase emission. By definition,

$$X = \frac{[TEQ_P]_{stack} + [TEQ_G]_{stack}}{[TEQ]_{ESP} + [TEQ]_{stack}} \approx \frac{[TEQ_P]_{stack}}{[TEQ]_{ESP}} + \frac{[TEQ_G]_{stack}}{[TEQ]_{ESP}} \quad (27)$$

Subscripts P and G indicate particulate and gas phase, respectively. 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 fuel [1]. For example, an early study [35] reported that 94% of the PCDD/Fs formed in a salt-laden hog power boiler were removed with the ash scrubbed out of the flue gas. The particulates in the stack and ESP may carry different concentrations of TEQs in ng/g [1]. However, it is reasonable to assume that stack dioxin emissions with the particulate phase are proportional to stack particulate emissions. Then, the first term on the right hand side of Equation (27) can be expressed as

$$\frac{[TEQ_P]_{stack}}{[TEQ]_{ESP}} = \lambda(1 - \text{Eff}_{ESP}) \quad (28)$$

where Eff_{ESP} represents the ESP particulate removal efficiency and λ is a coefficient, accounting for the difference in dioxin concentrations between ESP ash and stack particulate. The contribution due to gas phase emissions is determined by the volumetric flow rate of the flue gas and the PCDD/Fs vapor partial pressure. Then, the second term is given as

$$\frac{[TEQ_G]_{stack}}{[TEQ]_{ESP}} = \frac{P_{TEQ} \cdot GV_{stack}}{\text{ConC}_{TEQ} \cdot \text{AF}_{ESP}} \quad (29)$$

where P_{TEQ} represents the partial pressure of PCDD/Fs in the flue gas, ConC_{TEQ} the concentration of PCDD/Fs in the ESP ash (ng/g), GV_{stack} is the flue gas flow rate, and AF_{ESP} is the ESP ash flow rate. The latter three parameters can be measured, while the partial pressure may be estimated. It is assumed that equilibrium is established in the ESP between the vaporized PCDD/Fs and the PCDD/Fs condensed or adsorbed on the solid particles due to the long retention times (ie. minutes) typical for captured dust. The equilibrium vapor pressure increases with the ESP temperature according to the following thermodynamic equation:

$$RT_{ESP} \ln P_{TEQ} = -\Delta G_{TEQ}^{\circ} \quad (30)$$

where ΔG_{TEQ}° is the free energy change at the standard state for desorption of PCDD/Fs from ash particles, R the gas constant, and T_{ESP} is the ESP outlet temperature. Similarly, expressions equivalent to (27)-(30) may be obtained for V . Assuming that the free energy change for desorption of PAHs is approximately equal to ΔG_{TEQ}° , then X/V becomes a constant.

$$X/V = \eta \quad (31)$$

Inserting Equations (27)-(31) into Equation (26) yields

$$[\text{TEQ}]_{\text{stack}} = [\text{TEQ}]_{\text{non}} \cdot \lambda(1 - \text{Eff}_{\text{ESP}}) + \quad (32)$$

$$[\text{TEQ}]_{\text{non}} \cdot \frac{\exp\{-\Delta G^{\circ}_{\text{TEQ}}/(RT_{\text{ESP}})\} \cdot \text{GV}_{\text{stack}}}{\text{Conc}_{\text{TEQ}} \cdot \text{AF}_{\text{ESP}}} + \eta \cdot \text{K}(T_m) \cdot \tau \cdot [\text{PAH}]_{\text{stack}} \cdot [\text{HCl}]^2$$

A higher ESP outlet temperature reflects higher temperatures in the economizer, air heater, multi-cyclones, and ESP. An increase in these temperatures would result in a shift of the *de novo* zone towards the ESP, or towards the economizer, possibly, without much change in the overall *de novo* kinetics and reaction rate. With this consideration, as a first approximation, we may treat $\eta \cdot \text{K}(T_m) \cdot \tau$ as a constant.

For power boilers burning salt-laden hog fuel, the HCl concentration depends not only on the hog salt content, but, as shown by reactions (1-5), also on hog firing rate, fuel sulfur content, and ash properties. Nevertheless, the HCl concentration is assumed to be proportional to the hog salt content in this paper, implying that the combined effect of the other parameters is taken as a constant. This enables Equation (32) to be further simplified into

$$[\text{TEQ}]_{\text{stack}} = A + B \cdot \exp(-C/T_{\text{ESP}}) + D \cdot [\text{PAH}]_{\text{stack}} \cdot [\text{NaCl}]_{\text{hog}}^2 \quad (33)$$

where A, B, C and D are four 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 particulate control efficiency. The second term represents the gas phase emissions and is a function of the ESP outlet temperature. The third term is related to *de novo* synthesis.

Since the equilibrium vapor pressure increases with temperature, gas phase emissions of PCDD/Fs will increase with the ESP (or stack) temperature. This tendency may not be affected very much by the PCDD/Fs formation rate, if equilibrium is maintained in the ESP, because there is usually a much larger PCDD/Fs pool on the ash particles in the ESP. Particulate phase stack emissions of PCDD/Fs depend on the PCDD/F formation rate as well as the ESP efficiency. Although a variation of ESP temperature may not affect the ESP particulate removal efficiency, increased ESP temperature could cause the *de novo* formation rate in the ESP to increase. However, this increase in the *de novo* rate in the ESP has only a secondary effect on stack PCDD/F emissions when the ESP operates with high efficiency.

Model Validation, Data Correlation and Discussion

Although the 16 PAH species that are reported in the Canadian National Pollutant Release Inventory (NPRI) were analyzed in most of the stack tests covered in this study, only the high molecular weight (HMW) PAH species (those with ≥ 4 rings in the molecular structures) are included in calculating $[\text{PAH}]_{\text{stack}}$ in Equation (33). Mill F had 16 stack test results with the stack temperature, stack HMW PAH emissions and hog salt content also measured. One of the tests

had very high PAH emissions, with $7.2 \mu\text{g}/\text{m}^3$ at 11% O_2 HMW PAHs, as compared to an average of $0.56 \mu\text{g}/\text{m}^3$ at 11% O_2 for the other 15 tests. The very high PAH emissions indicated poor combustion conditions and possibly significant precursor dioxin formation. As mentioned earlier, the present version of the model, as represented by Equation (33), cannot be applied to such a case and that datum was not included in the model validation. The correlation of the 15 test results with Equation (33) is shown in Figure 6. 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.

The stack emission model was further verified with test data obtained on all of the 6 power boilers with a dry ESP covered by this study. Results from the two boilers with wet scrubbers, Boilers A and H, are not included in the verification database. The 6 boilers had a total of 68 stack tests with the stack temperature, stack HMW PAH emissions and hog salt content also measured. Four of the 68 tests had very high PAH emissions: $7.2 \mu\text{g}/\text{m}^3$ HMW PAHs (Mill F), $27.1 \mu\text{g}/\text{m}^3$ HMW PAHs (Mill D), 22.2 and $35.5 \mu\text{g}/\text{m}^3$ HMW PAHs (Mill G), all at 11% O_2 . Very poor combustion conditions were observed in two additional tests (Mill G) with low hog steam loads (40-44% of hog MCR). Although the measured stack PAH emission levels were not as high as those in the above 4 results, the PCDD/F emissions were beyond the range (up to $1.2 \text{ ng TEQ}/\text{m}^3$ at 11% O_2) used in graphing the test results. Significant precursor dioxin formation is believed to have occurred in these 6 tests, as discussed previously [4, 5]. Again, the present version of the model, as represented by Equation (33), is not suitable for modeling high levels of precursor PCDD/F formation. Thus, the intermill verification database contains a total of only 62 data points.

Figure 7 shows the intermill data correlation with Equation (33) based on single tests, while Figure 8 uses only the averages from duplicate and triplicate tests. Good agreement between the experimental data and the model is shown in both figures. The correlation coefficient is improved when using the averages for the duplicate/triplicate tests as this also reduces the data scatter. It should be noted that where the ESP outlet temperature was not available, the stack temperature was used. 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/mole at ESP temperatures. The magnitude of this figure seems to be reasonable, and compares favorably with the range of 45 to 53 kJ/mole provided by Altwicker *et al.* [22] for the PCDD/F solid-to-gas desorption step.

Everaert and Baeyens [10] found that stack TEQ emissions from the municipal solid waste incinerators they studied could be correlated to ESP temperature by the function $0.001\text{exp}(0.0368T)$, where T is in °C. Both this literature correlation and Equation (33) predict TEQ emissions increasing exponentially with ESP temperature, although the literature correlation is purely empirical and substantially overestimates TEQ emissions measured on the salt-laden hog fuel power boilers at the BC coastal pulp mills.

Equations (22-26) indicated that the PCDD/F formation rate by de novo reactions increases exponentially with the de novo zone temperature. However, after a series of simplifications, the reaction temperature, T_m , is absent in Equation (33). This effect is, therefore, evaluated in Figure 9 by correlating stack emissions with the average air heater inlet temperature. The air heater temperature was selected because the residence time for the flue gases in the air heater is typically very much longer than the residence time in other heat exchanger banks. The long residence time in the air heater provides time for de novo formation of dioxins and the rate of de novo formation might, therefore, be expected to correlate best with the air heater temperature. In Figure 9, there is one data point for each mill, representing averaged test results for the mill, except for Mill C and Mill H. Mill C has two points, one representing normal operations and the other representing operations with increased steam pressure and temperature. No point is present in the figure for Mill H, because of the special feature of the boiler with direct contact between the flue gas and hog fuel in the hog dryer. Also, results obtained in water spraying tests are excluded in averaging the data for Mill F. The correlation seems fairly good ($R^2 = 0.55$), indicating that stack dioxin emissions increase exponentially with the air heater inlet temperature, as predicted by reactions (22-24).

The 8 data points shown in Figure 9 are compared with two points obtained on two pilot scale fluidized bed combustors, operated by UBC [7] and CANMET [36], respectively. Both pilot facilities were equipped with baghouse filters.

About 20 combustion tests were conducted at UBC under the present research project. No stack dioxin emissions were tested and only ash samples were analyzed. The results showed generally very low levels of PCDD/F formation. This is attributed to the low flue gas temperatures at the baghouse inlet as a result of a powerful water-jacketed, heat exchanger. In order to compare the UBC results with mill stack results, we assumed that stack dioxin emissions from this pilot facility were close to the lower end of the mill emission results and arbitrarily took 0.012 ng TEQ/m^3 at 11% O_2 as average. The baghouse inlet temperature was taken as the "air heater inlet temperature".

Dioxin tests on the CANMET pilot facility were carried out in 1995-96. The emission levels of PCDD/Fs from this facility were very high, except for those few tests where the flue gas was quenched by a water-jacketed flue gas cooler. In the absence of the cooler, the flue gas was slowly cooled to the baghouse temperatures only by heat losses from uninsulated flue gas pipes. These pipes may be regarded as "air heater tubes" and hence the high temperature at the flue gas cooler bypass inlet is regarded as the "air heater inlet temperature" for this facility.

As shown in Figure 10, dioxin emission levels tested on the hog fuel power boilers at the BC coastal mills were lower than those from the CANMET combustor but higher than those from the UBC facility. An improved correlation was obtained with the extended database including all the facilities. It again shows that TEQ formation levels increase exponentially with increasing air heater temperatures. These findings are consistent with the literature theories of de novo formation of PCDD/Fs, as well as with reactions (22-24) of the present model. Further to the discussions provided in [5], this model can also explain why dioxin emissions from some of the facilities (boilers and pilot plants) are consistently higher than those from the others:

- UBC's very low dioxin levels were caused by flue gas quenching from $>550^{\circ}\text{C}$ to the baghouse temperatures ($<250^{\circ}\text{C}$) using their water-jacketed heat exchanger.
- CANMET's very high dioxin levels were mainly due to the slow, natural cooling of their flue gas travelling in the pipeline (gradual heat losses). In contrast, in those few tests where the flue gas was quenched by their water-jacketed flue gas cooler, the dioxin levels were reduced from 22 to 0.5 ng TEQ/m^3 .
- The air heater inlet temperature was up to 417°C for Mill C, 407°C for Mill F, and up to 303°C for Mill E. To a large degree, these temperature differences determined that Mill C has the highest dioxin emissions and Mill E the lowest.
- The full model would suggest that lowering the ESP temperature alone could only solve the dioxin problem partially, but not completely. Lowering the air heater temperature, for example by placing an effective economizer before the air heater, should be a better solution. In particular, a colder air heater would usually also result in a colder ESP.
- Good combustion always matters for dioxin control. Combustion conditions are, to a great degree, responsible for variations of dioxin emissions measured on a specific boiler. However, the current version of the model is not suitable for description of dioxin emission variations caused by precursor reactions.

SUMMARY

This paper has presented a thermodynamic analysis of high temperature salt chemistry. Its influence on dioxin and furan formation in power boilers burning salt-laden wood waste was examined through the relationships between Cl_2 , HCl , NaCl (g) and NaCl (c) . The following conclusions can be drawn from that analysis:

- Hog salt evaporates nearly completely during combustion to form gaseous NaCl
- HCl and Cl_2 are not products of combustion of salt-laden wood waste but form when sulfur is burned with even ash-free hog fuel. In comparison, HCl is a product of combustion of PVC -laden municipal solid waste.
- NaCl can be converted to HCl by reactions with SO_2 or alumina-silicate materials.
- HCl can be catalytically oxidized by O_2 to Cl_2 , a strong chlorinating agent for PCDD/F formation.
- Cl_2 can be reduced back to HCl by oxidizing SO_2 .
- The presence of sulfur at low concentrations enhances PCDD/F formation by increasing HCl concentrations.
- The presence of sulfur at high concentrations inhibits de novo formation of PCDD/Fs through Cl_2 reduction by excess SO_2 .
- The maximum theoretical molar ratio of Cl/S required for an inhibiting effect is 2 for power boilers burning salt-laden hog fuel.
- NH_3 can reduce Cl_2 to HCl , and therefore, may inhibit de novo formation of PCDD/Fs . Nitrogen oxide does not have any effect on de novo formation of dioxins and furans. The effect of carbon monoxide on dioxin and furan formation cannot be determined by thermodynamic analysis alone.

A kinetic model was proposed, describing the PCDD/F formation rate in power boilers burning salt-laden wood waste. A simplified version of that model forms a stack emission model. The

stack emission model was verified with both intra-mill (Mill F) and inter-mill (6 mills) test data. The following conclusions were drawn:

- The kinetic model, which is semi-empirical, considers both precursor and de novo formation mechanisms and also incorporates the results of our thermodynamic analysis.
- Good combustion always matters for dioxin control. The stack emission model assumed a constant formation rate from precursor reactions and should only be applied to tests with good combustion conditions.
- Stack PCDD/F levels are not necessarily correlated to ash PCDD/F concentrations.
- Stack dioxin emissions increase linearly as the ESP efficiency decreases, exponentially with increasing ESP temperature, and to the second order with hog salt content.
- Stack dioxin emissions also increase exponentially with increases in the air heater inlet temperature. Both mill-averaged test results and those obtained on two pilot-scale combustors support this correlation.

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NOMENCLATURE

- A, B, C, D = Model parameters, to be estimated
 A_i = Pre-exponential factor of the rate constant of reaction i
 BFB = Bubbling fluidized bed
 E_i = Activation energy of reaction i
 ESP = Electrostatic precipitator
 GB = Generating bank
 HCs = Hydrocarbons
 Hog fuel = Bark and wood waste
 k_i = Rate constant of reaction i
 LOI = Loss on ignition
 MC = Multi-cyclones
 MCR = Maximum Continuous Rating for steam generation
 ng = nanogram (10^{-9} g)
 OCs = Organic compounds
 PAHs = Polycyclic (polynuclear) aromatic hydrocarbons (only the 16 species as required by the National Pollutant Release Inventory of Canada are included for this study)
 PCDDs = Polychlorinated dibenzo-p-dioxins
 PCDFs = Polychlorinated dibenzofurans
 PM = Particulate matter

PRECs = PCDD/F formation precursors

P_{TEQ} = Vapor pressure of PCDD/Fs

R = Gas constant

t = Time

T = Temperature

T_m = weighted mean reaction temperature

TEF = Toxicity equivalent factor of dioxins/furans

TEQ = Toxicity Equivalent to 2,3,7,8-tetra-chlorinated dibenzo-p-dioxin

= $\sum\{(TEF)_i \cdot C_i\}$, where $(TEF)_i$ is the NATO TEF of congener i, C_i is its concentration.

V = Fraction of formed PAHs escaping to the stack

X = Fraction of formed PCDD/Fs escaping to the stack.

[S] = Concentration of species S

ΔG = Chemical free energy change under specified conditions

ΔG° = Chemical free energy change at the standard state

τ = Reaction time or residence time

η, λ = coefficient

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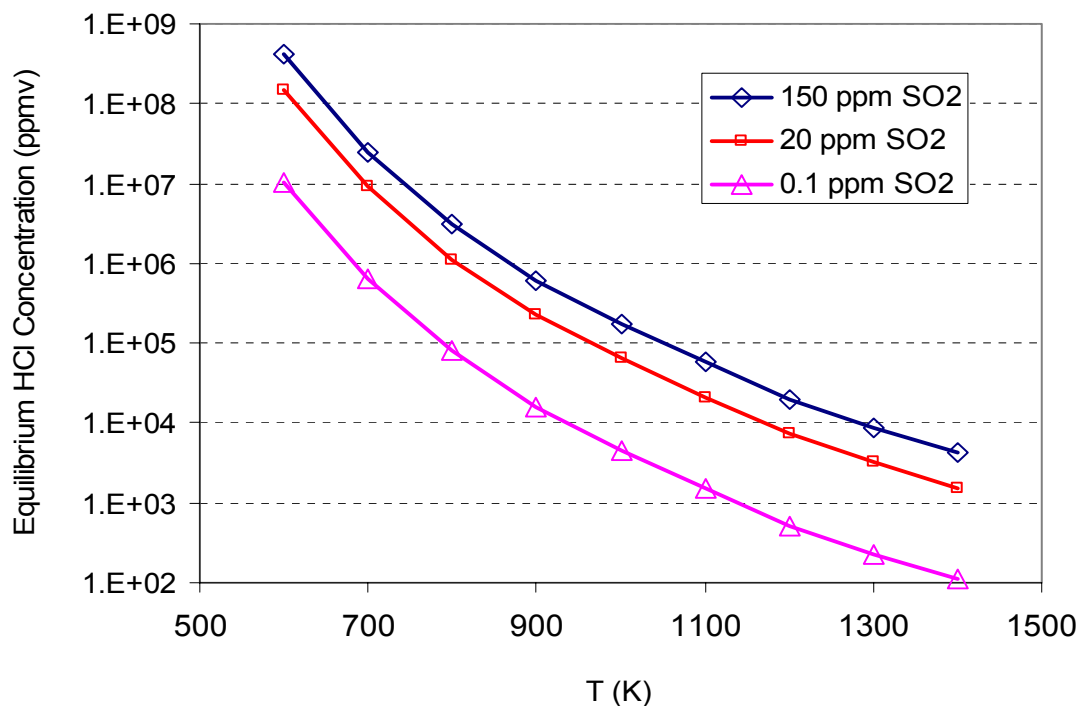


Figure 1. Equilibrium gas concentrations calculated for the reaction:
 $2\text{NaCl} + \text{SO}_2 + \text{H}_2\text{O} + 1/2 \text{O}_2 = \text{Na}_2\text{SO}_4 + 2\text{HCl}$, at 20% H_2O and 10% O_2 .

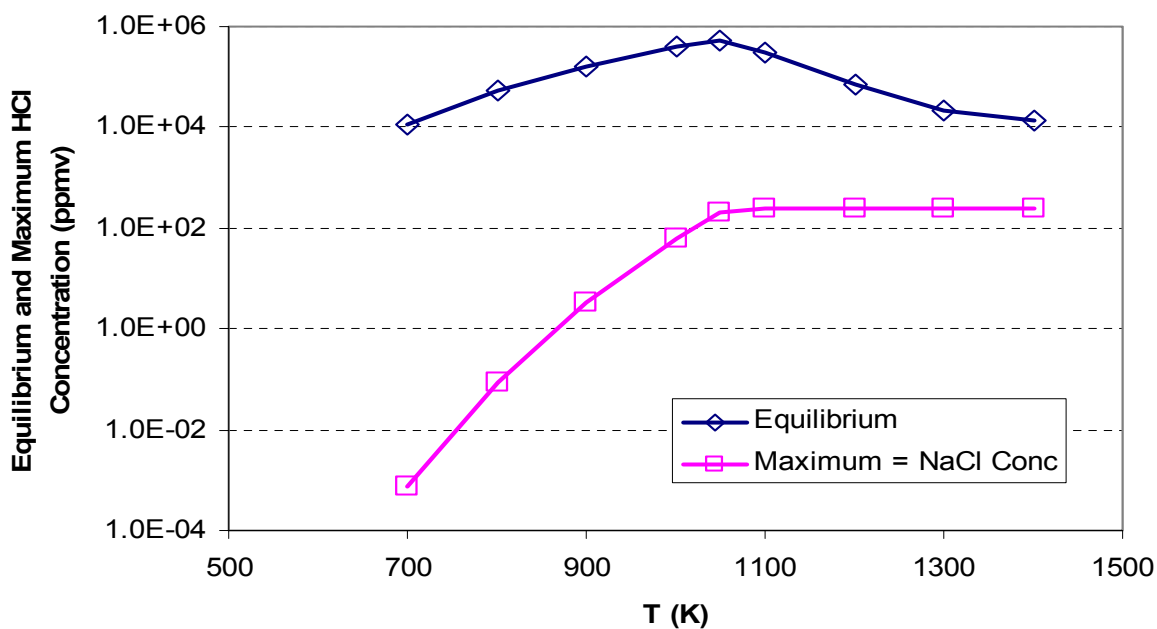


Figure 2. Equilibrium gas concentrations calculated for the reaction:
 $\text{NaCl} + 5/2 \text{SiO}_2 + 1/2 \text{Al}_2\text{SiO}_5 + 1/2 \text{H}_2\text{O} = \text{NaAlSi}_3\text{O}_8 + \text{HCl}$,
 with 0.47% NaCl in hog; 20% H_2O and 10% O_2 in flue gas [27, this work].

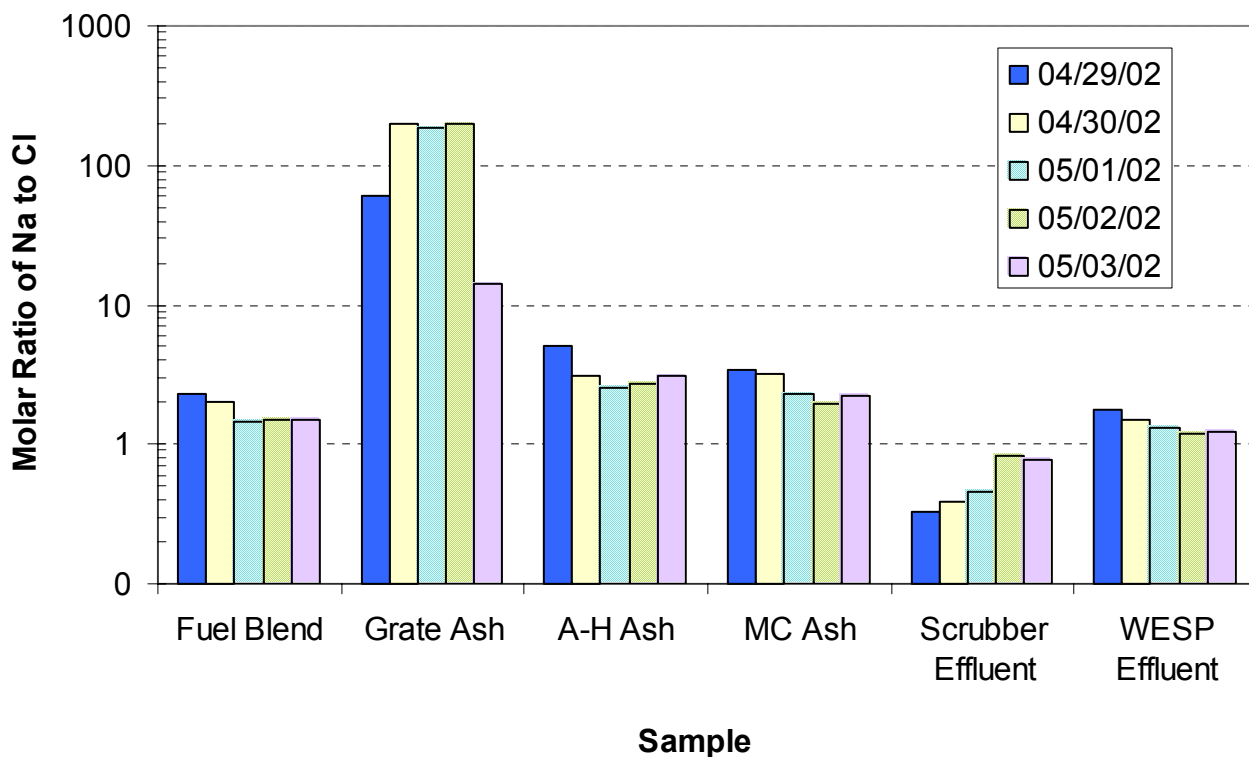


Figure 3. Distribution of Na and Cl in the fuel and in different ash streams for Boiler A.

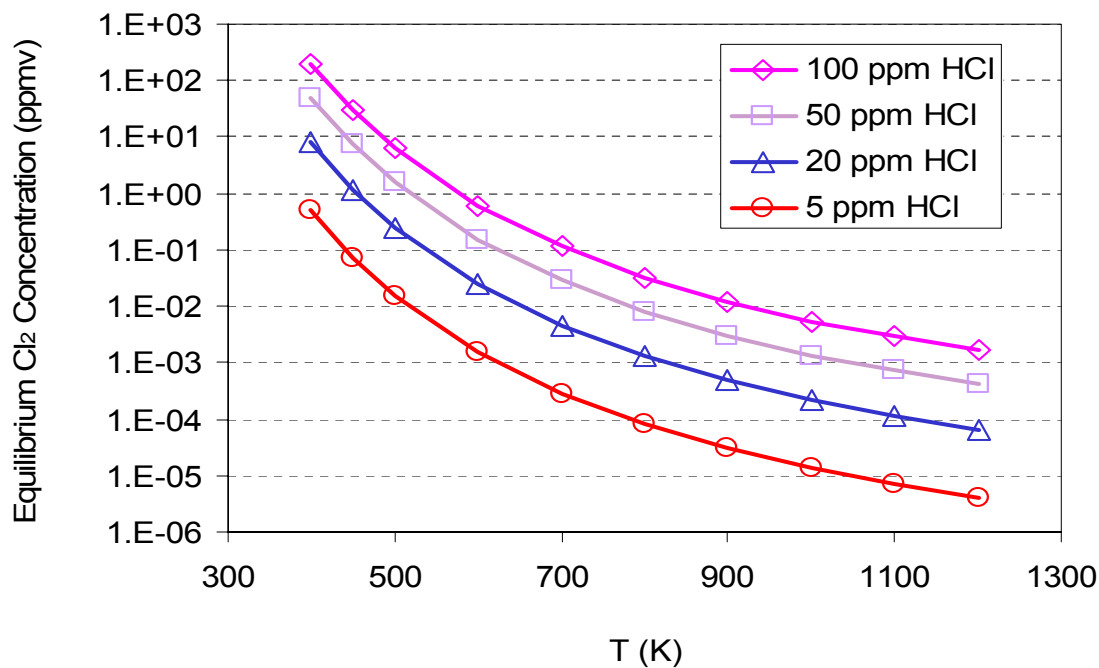


Figure 4. Equilibrium gas concentrations calculated for the reaction:
 $2\text{HCl} + \text{O}_2 = \text{Cl}_2 + \text{H}_2\text{O}$, at 20% H_2O and 10% O_2 .

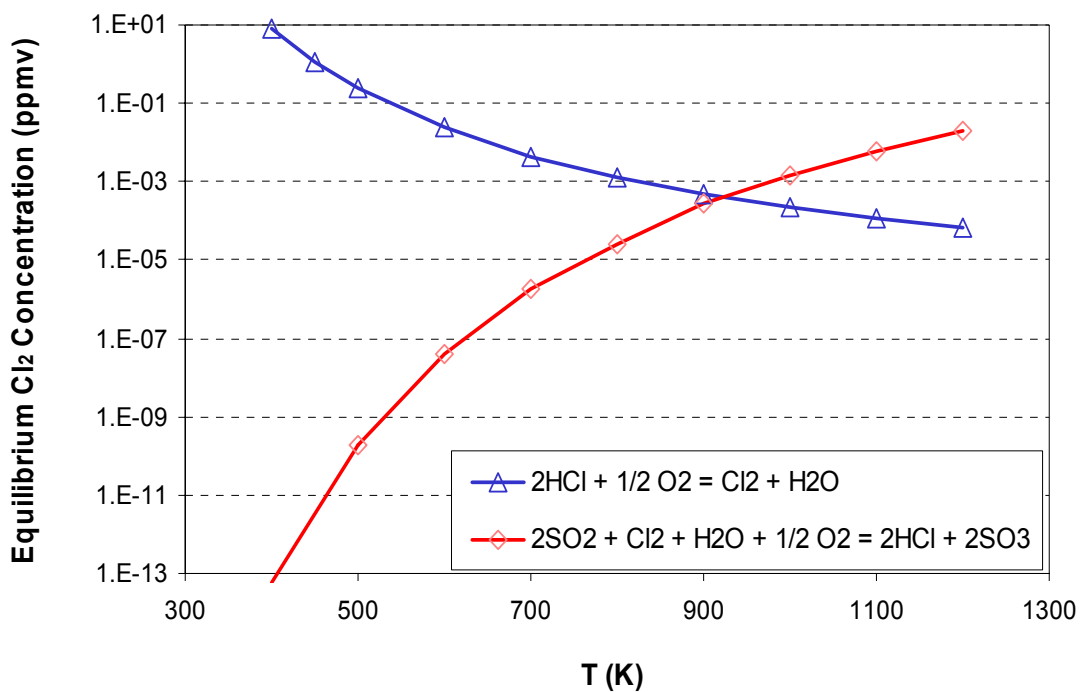


Figure 5. Equilibrium Cl_2 concentration calculated for the sulfur reaction and the Deacon Reaction at 20% H_2O , 10% O_2 , with 20 ppm HCl, and with equal SO_2 and SO_3 .

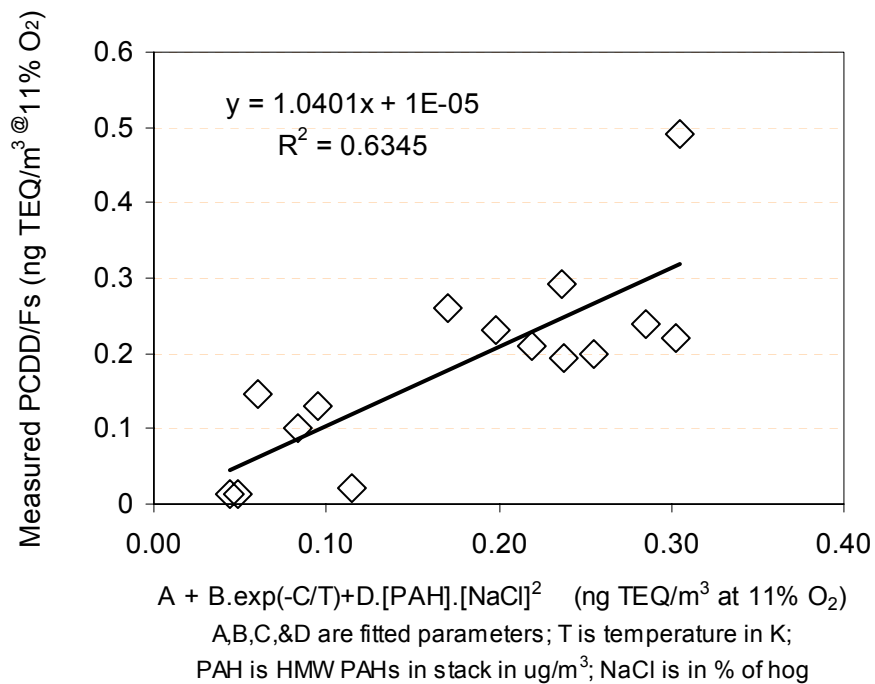


Figure 6. Validation of stack dioxin emission model with test data from Mill F.

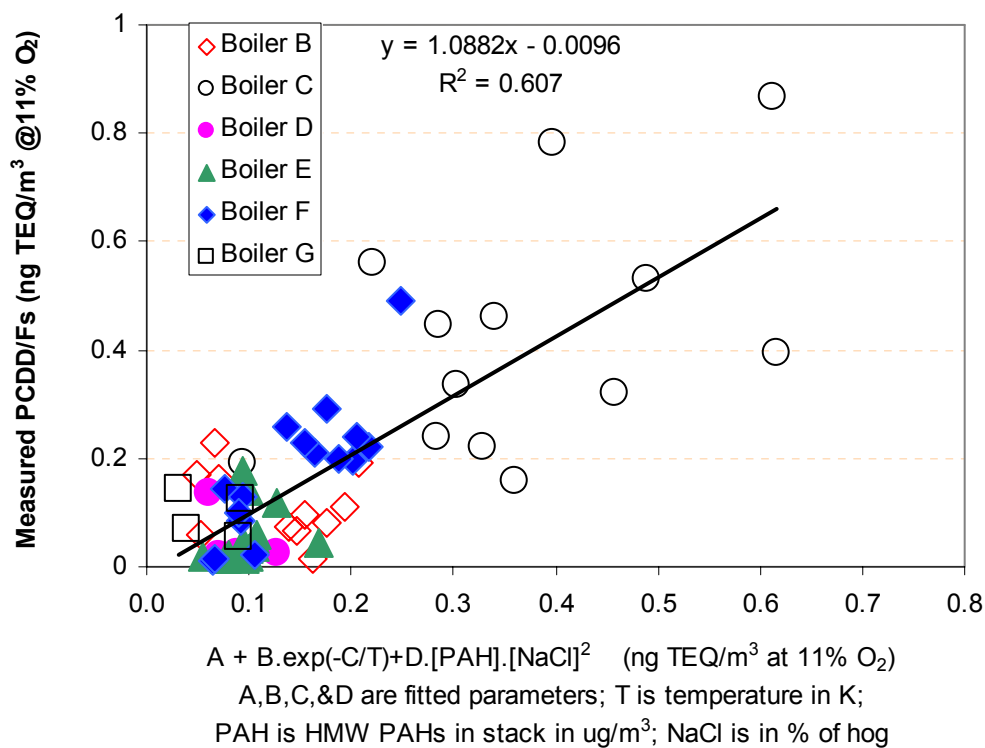


Figure 7. Intermill data correlation based on single stack tests.

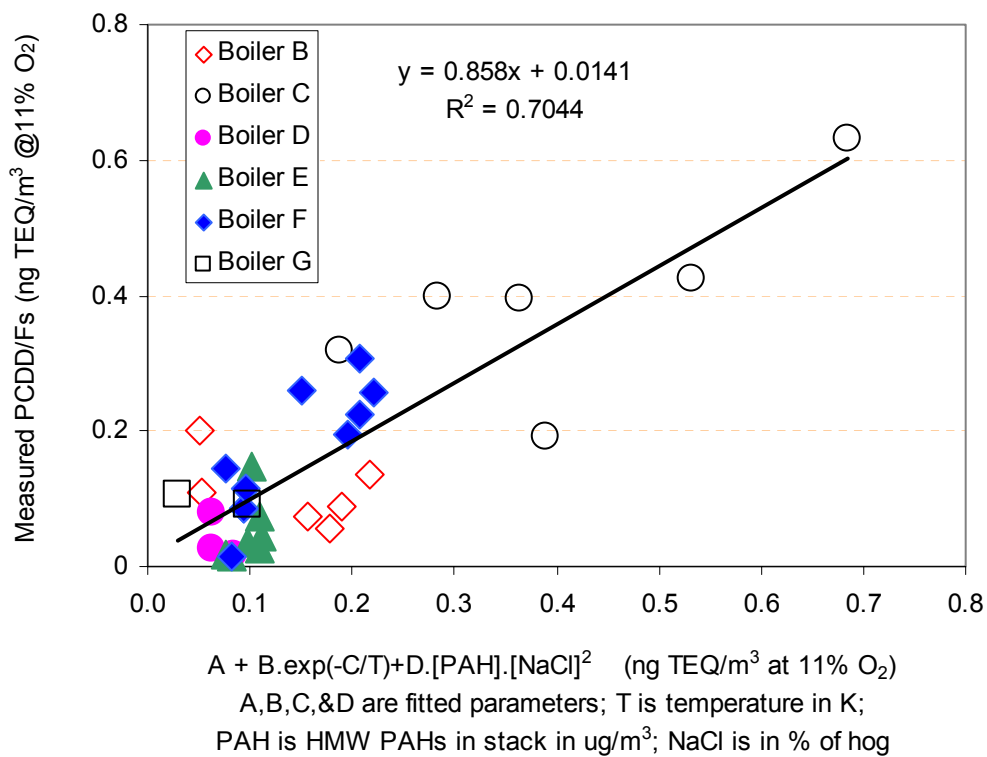


Figure 8. Intermill data correlation based on duplicate and triplicate stack tests.

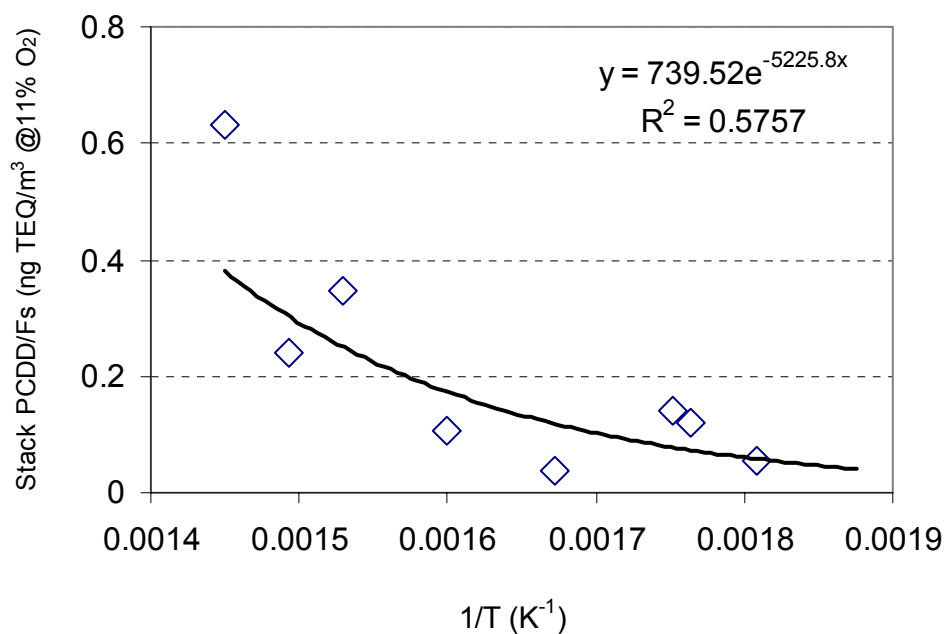


Figure 9. Correlation of stack emissions with average air heater inlet temperatures.

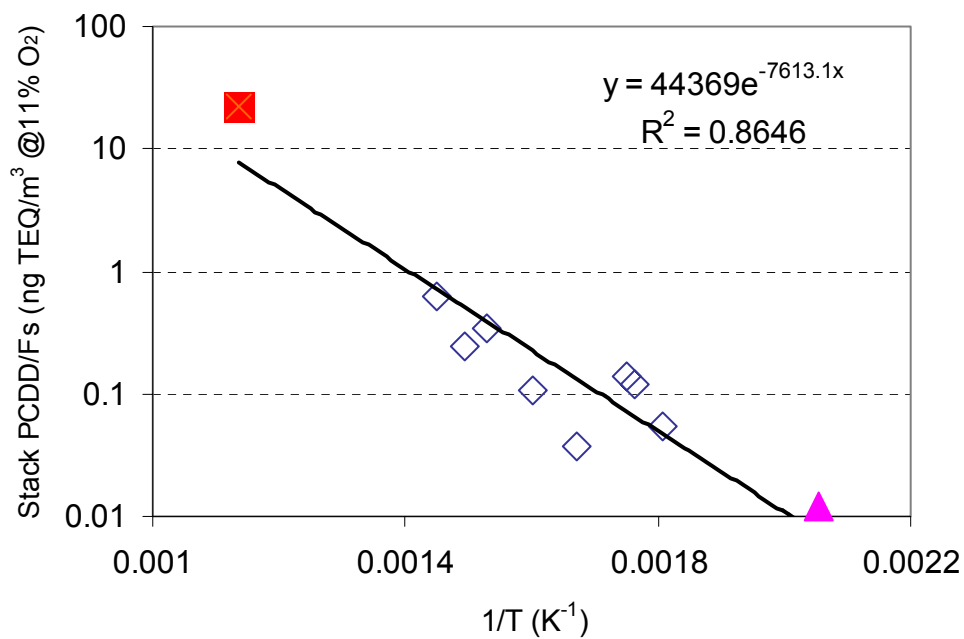


Figure 10. Effect of average air heater inlet temperatures on stack dioxin emissions and correlation of mill test data with pilot plant experimental results. \diamond = mill data; \blacksquare = CANMET data; \blacktriangle = UBC data