Research is conducted to evaluate and quantify the effect of mixing coal with municipal solid waste (MSW) in incinerators in reducing the emissions of chlorinated organics, especially polychlorinated dibenzo-p-dioxins and furans (PCDDs and PCDFs). The research was performed over a twelve-month period, consisting of three phases; Phase I, bench-scale reactor system with a simulated MSW combustion environment; Phase II, pilot-scale reactor system with coal/natural gas combustion and MSW fly ash in a simulated MSW combustion environment; and Phase III, follow up testing. The research is aimed at quantifying the effects of coal sulfur, determining the mechanism and kinetics of deactivation, and potentially identifying coal-MSW co-firing conditions most effective in reducing the emissions of PCDD/PCDF.

Pilot-scale tests in the Innovative Furnace Reactor (IFR) involved injection of MSW fly ash samples into the duct and downstream sampling for dioxins/furans. Results of these tests reaffirm our past finding that SO$_2$ reduces PCDD/PCDF levels; they also indicate that this effect is independent of SO$_2$ injection temperature. The maximum sulfur-to-chlorine ratio at which substantial inhibition takes place, based on tests with different fuels, is found to be 1.15 for the pilot-scale tests. For formation of PCDD/PCDF, effect of gas-phase precursor concentration is shown to be significant; on the other hand, MSW fly ash feed rate, and hence the concentration of catalytic sites, does not affect the yield.

Bench-scale tests examined some of the possible sulfur inhibition mechanisms. While poisoning of the copper catalyst is known to be a dominant, this work shows that SO$_2$, also reacts with molecular chlorine, produced catalytically from HCl via the Deacon process, converting it back to the less reactive HCl. The MSW fly ash has a strong affinity towards HCl, which would favor the eventual PCDD/PCDF formation.
EXECUTIVE SUMMARY

The Air and Energy Engineering Research Laboratory (AEERL) of the United States Environmental Protection Agency (EPA) has proposed co-funded research in conjunction with the Illinois Clean Coal Institute (ICCI) to evaluate and quantify the reduction of pollutant emissions by mixing coal with municipal solid waste (MSW) in incinerators. Previous research under this program has shown that sulfur, when present in a combustion environment, can inhibit the formation of polychlorinated dibenzo-p-dioxins and furans (PCDDs and PCDFs). Due to their sulfur content, co-firing of Illinois coal with MSW is a viable option for controlling emissions of chlorinated organic compounds. Establishing co-firing criteria and information on most effective conditions for reductions in emission levels are necessary to demonstrate that use of Illinois coals is a commercially attractive option for MWC (municipal waste combustor) industry.

The objectives of the research are to perform tests (both bench-scale and pilot-scale) using simulated MSW combustion environments to evaluate the effects of coal sulfur in inhibiting the formation of PCDDs and PCDFs. The proposed research is aimed at quantifying the effects of coal sulfur, determining the mechanism of deactivation, and potentially identifying coal-MSW co-firing conditions most effective in reducing the emissions of chlorinated organic compounds. The research will be performed over a twelve-month period and will consist of three phases; Phase I, bench-scale reactor system with a simulated MSW combustion environment; Phase II, pilot-scale reactor system with coal/natural gas combustion and MSW fly ash in a simulated MSW combustion environment; and Phase III, follow up testing. If successful, the proposed research will provide guidelines for co-firing of coal with MSW so that emissions are reduced in a cost-effective fashion.

Pilot-scale tests in the Innovative Furnace Reactor (IFR) involved injection of MSW fly ash samples into the duct and downstream sampling for dioxins/furans. Results of these tests reaffirm our past finding that SO₂ reduces PCDD/PCDF levels; they also indicate that this effect is independent of SO₂ injection temperature. The maximum sulfur-to-chlorine ratio at which substantial inhibition takes place, based on tests with different fuels, is found to be 1.15 for the pilot-scale tests. For formation of PCDD/PCDF, effect of gas-phase precursor concentration is shown to be significant; on the other hand, MSW fly ash feed rate, and hence the concentration of catalytic sites, does not affect the yield. Bench-scale tests to examine possible sulfur inhibition mechanisms show that SO₂ reacts with molecular chlorine, produced catalytically from HCl via the Deacon process, converting it back to the less reactive HCl.
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OBJECTIVES

The specific goals of the research are to quantify the effects of coal combustion, role of sulfur in particular, in the formation and control of chlorinated organics (primarily PCDD/PCDF). Phase I tests will be in a bench-scale short time reactor, with fly ash and additives injected to simulate municipal solid waste (MSW) combustion. These tests will identify the mechanism and kinetics of sulfur inhibition in the PCDD/PCDF formation. Phase II testing will be in a pilot-scale furnace and will involve coal/natural gas firing with additives to closely simulate process conditions for combined coal/MSW combustion. These tests will not only quantify the inhibitory effects of S on formation, but will also examine other potential impacts of typical combustion environments. Depending on the results obtained from these two phases, Phase III tests will be carried out in either or both the test facilities to close important knowledge gaps. Specifically, the objectives of the research are:

- To perform bench- and pilot-scale laboratory tests to identify conditions under which co-firing coal and MSW decreases formation of chlorinated organics
- To measure the effect of sulfur and other process parameters related to combined coal-MSW combustion on chlorinated organics formation
- To determine the mechanism of sulfur inhibition in chlorinated organic formation
- To investigate the kinetics of inhibition

INTRODUCTION AND BACKGROUND

Significant amounts of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) have been detected in the emissions of municipal waste combustors (MWCs). This, however, does not appear to be the case with coal-fired combustors. It follows that, although chlorine (Cl) and organic ring structures are present in both systems, the coal combustion environment is not conducive to PCDD/PCDF formation, and hence, co-firing MWCs with coal may discourage their formation.

Griffin (1986) suggested that \( \text{SO}_2 \) converts the active Cl, to HCl, leading to reduced PCDD/PCDF formation:

\[
\text{SO}_2 + \text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \text{SO}_3
\]  \hspace{1cm} (1)
Recently, Lindbauer et al. (1992) reported that co-firing a MSW incinerator with 60% coal drastically reduced the PCDD/PCDF levels, presumably due to sulfur. Fouling of the Cu catalyst by sulfur species appears to be a dominant mechanism of inhibition (Gullett et al. 1992). Last year's work in our laboratory, funded by ICCI, involved tests with both IBC-109 coal- and natural gas-fired environments. The results revealed that:

- Combustion of the coal tested, at low or moderate HCl concentrations, formed very little PCDD/PCDF;
- Inorganic sulfur (present as SO₂) can significantly reduce PCDD/PCDF formation, and such reduction is possible at sulfur-to-chlorine ratio as low as 0.64;
- At a low S/Cl ratio, however, if the HCl concentration is high, the addition of coal can actually increase the PCDD/PCDF yield.

Thus, it is clear that co-firing MWCs with coal can reduce PCDD/PCDF emissions. However, it is critical to choose appropriate coal type and co-firing conditions to achieve positive results. A better understanding of the formation and inhibition mechanisms and parametric studies of the reaction variables (e.g., S/Cl ratio) are important steps for establishing guidelines for co-firing MWCs with coal.

The research performed involves tests (both bench-scale and pilot-scale) using simulated MSW combustion environments to evaluate the effects of coal sulfur in inhibiting the formation of PCDDs and PCDFs. The work is aimed at quantifying the effects of coal sulfur, determining the mechanism and kinetics of deactivation, and potentially identifying coal-MSW co-firing conditions most effective in reducing the emissions of chlorinated organic compounds.

**EXPERIMENTAL PROCEDURES**

**REACTOR SYSTEMS**

The experimental systems used are (1) pilot-scale Innovative Flow Reactor (IFR), and (2) bench-scale Chlorinated Organics Reactor. These set up are described briefly below.

**(1) Innovative Furnace Reactor (IFR):**

The pilot unit used in this project is EPA AEERL's Innovative Furnace Reactor (IFR), with the overall schematic shown in Figure 1. The IFR is a down-fired, refractory-lined cylindrical unit with a length of about 3 m; For the earlier furnace tests under this project, the internal diameter of the furnace was 15.2 cm. Subsequently, the furnace was upgraded
to a diameter of 20.3 cm. The facility is nominally rated at 120,000 Btu/hr on either a gaseous fuel or pulverized coal. Ports along the length of the IFR facilitates addition of reactants or sampling. The unique design of the furnace allows for staging of combustion to simulated various applications, including MSW combustion. Continuous emission monitors are provided to measure CO, CO₂, O₂, SO₂ and NOₓ. The MSW fly ash sample tested was from an electrostatic precipitator hopper on a full-scale mass-burn facility at Quebec City, Canada, prior to facility modifications for improved combustion. The as-received fly ash was fed into the furnace by a K-Tron feeder.

Furnace emissions were sampled in the downstream duct section of the IFR and passed through heated sample lines to continuous emission monitors (CEMs). Gases analyzed for CO₂, O₂, and CO were first passed through a gas dryer and a desiccant canister of anhydrous CaSO₄. All of the above on-line CEMs are zeroed and spanned with gases of known concentration both before and after each daily trial. HCl concentration in the furnace was determined used EPA Method 26 protocol.

Organics (PCDD/PCDF) were sampled separately from the duct using isokinetic sampling protocols and EPA MM5 sampling trains. These trains consist of a quartz sampling probe, followed by a filter, XAD trap, and impingers. The probe rinse, filters, and XAD were analyzed together for PCDD/PCDF congeners.

IFR tests involved both natural gas and coal firing. The natural gas tests were conducted at HCl concentrations of about 450 ppm to compare with the previous results (>1100 ppm). The parameters that were varied in the tests are as follows:

- SO₂ injection temperature. Results were compared between SO₂ injection near the burner and at the end plate (about 400°C).
- Gas-phase precursor concentration. To vary this parameter, part of the combustion air was injected into the IFR through one of the lower ports. This caused fuel-rich conditions at the burner, and the staged air at the lower port resulted in low-temperature (<1000°C) combustion. Thus, poor burn conditions were in effect, increasing the concentration of unburnt hydrocarbons in the flue gas. This would, in turn, increase aromatic ring structures which are precursors for PCDD/PCDF synthesis.
- Condensed organics on MSW fly ash surface. The raw fly ash was extracted to remove all the condensed organics and the extracted fly ash was injected into the furnace.
Catalytic sites on MSW fly ash surface. The MSW fly ash feed rate was reduced from 111 to 60 g/hr. Since the PCDD/PCDF synthesis is known to be catalyzed by copper catalyst sites on the fly ash surface, varying the fly ash feed rate would alter the active site concentration.

In addition, the furnace was doped with SO₂, with no added HCl, and the PCDD/PCDF yield was determined. This run would compare with a previous test conducted under last year's program where significant PCDD/PCDF yield was noted even with no added HCl.

In the upgraded furnace (larger diameter), tests were conducted where the reactor was fired with a with a low-chlorine, medium-sulfur (2.6%) coal (Pittsburgh No.8) at 60,000 Btu/hr. In the coal-fired furnace, the effect of coal sulfur in PCDD/PCDF yield was examined. The S/Cl ratio was varied by varying the amount of HCl doped into the furnace. A coal blank test (without MSW fly ash injection) was also conducted with the furnace doped with HCl to determine if this coal combustion individually leads to dioxin formation.

(2) Chlorinated Organics Reactor (COR):

The COR was used previously used for S-inhibition studies on PCDD/PCDF formation (Gullett et al. 1992). The COR is a concentric tube, quartz reactor inserted into the horizontally mounted, single-zone, electric furnace. The solid sample is embedded in a quartz wool bed, placed in the inner tube of the reactor, and then heated to the test temperature. The composition of the process gas through the COR was 10% O₂, 1000 ppm HCl, and 1000 ppm SO₂ in N₂. Total gas flow rate was 1.33 L/min (STP). The COR effluent stream was passed through a Teco HCl analyzer to monitor the changes in HCl concentration. In these tests, 1 g of CuO was used for simulating MSW fly ash catalytic properties.

The COR tests used three different flow schemes as shown in Figures 2a, 2b and 2c. Under the first configuration (Figure 2a), effect of SO₂ pretreatment on the Deacon process reaction was tested. The CuO sample was pretreated for 30 min. under 1000 ppm SO₂. Then, HCl was introduced at 1000 ppm and the effect of SO₂ pretreatment on the Deacon process response observed by monitoring the outlet HCl concentration. This run was compared with that where pretreatment was without SO₂. Also tested using this scheme was the effect of MSW fly ash on the HCl concentration.

The second scheme (Figure 2b) was used to examine the relative effects of SO₂ between catalyst poisoning and depletion of gas-phase chlorine species. The CuO sample was placed at the end of the COR inner tube. HCl was introduced from the right,
into the inner tube. In one test, SO₂ entered along with HCl and hence, passed through the catalyst; in a companion test, SO₂ was introduced from the left, immediately after the catalyst. Thus, the former test measures the combined SO₂ effect on the Deacon process and the gas-phase Cl depletion, while the latter measures only the Cl depletion effect. Due to the transient nature of the response, the Deacon process was allowed to proceed for 60 or 90 min; then SO₂ was introduced for 60 min and then stopped to continue with the uninhibited Deacon process.

The third scheme (Figure 2c) was used to study the possible reaction between SO₂ and Cl₂. Since this reaction proceeds only in the presence of H₂O, moisture was introduced into the COR by bubbling nitrogen through a water bath. In these tests, the process gas composition was 10% O₂, 500 ppm Cl₂, and 1% H₂O in nitrogen. When added, the SO₂ concentration was 1000 ppm.

**SAMPLE ANALYSIS**

Samples from the IFR system are analyzed in AEERL’s in-house facilities by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS), using a Hewlett-Packard 5890/5970 Gas Chromatography/Mass Selective Detector (GC/MSD). The methodology is a slight adaptation of EPA Method 23 (1991) and RCRA Method 8280 (1986). Isotopically labelled internal standards for each congener class are incorporated during the extraction and clean up phases of the analytical procedures to enhance analytical accuracy. An internal standard was used that consisted of a 13C₁₂-labelled congener from each tetra-octa PCDD/PCDF (except for octa-CDF). The recovery standard 13C₁₂-labelled TCDD is added before injection on the GC. The recovery must be within 40–120% to be acceptable. Thus, the results obtained are levels of each tetra-octa PCDD/PCDF congener in the sample.

**RESULTS AND DISCUSSION**

**Pilot-scale results**

Figure 3 shows the PCDD/PCDF yield for MSW fly ash when no HCl was added to the IFR. Previous results (0 ppm SO₂) have shown that MSW fly ash contains surface chlorine in sufficient quantities to yield PCDD/PCDF. However, when the furnace was doped with SO₂ at 438 ppm, there was very little formation. Prior analysis has shown that the raw MSW fly ash does not contain any detectable PCDD/PCDF. Figure 4 shows results for two SO₂ injections: the furnace injection is at the burner and the end plate injection is at a nominal temperature of about
400°C. In both cases, the yield was reduced.

Effects of fly ash properties and burn conditions on PCDD/PCDF formation were examined. As discussed before, varying the feed rate of MSW fly ash would alter the concentration of available Cu-catalytic sites as well as the amount of condensed organics, extraction would remove condensed organics from the fly ash surface, and causing a poor burn would increase the gas-phase precursor concentration. The results are shown in Figure 5:

- The fly ash contributes to PCDD/PCDF formation by providing catalytic sites for the Deacon process and biaryl synthesis (Gullett et al. 1992), and as seen in Figure 3 through condensed organics on its surface. The fact that reducing the MSW fly ash feed rate by nearly half (110 to 61 g/hr) had little effect on the yield suggests that, for the MSW fly ash tested, the catalytic sites are in excess; also the contribution of condensed organics is small compared to those from the gas phase.

- Removing the condensed organics from the fly ash surface (extraction) has little effect on the yield. This again suggests that the contribution from surface condensed organics is minimal.

- The poor burn conditions nearly doubled the PCDD/PCDF levels. Since higher levels of aromatic hydrocarbons are expected under poor burn conditions, it appears that gas-phase precursor concentration is a controlling parameter for PCDD/PCDF formation.

The above tests were conducted in a natural-gas combustion environment. Pure SO₂ doped into the furnace was the sulfur source. However, in a coal-MSW co-fired process, the coal would provide the sulfur source. To determine if SO₂ produced from coal combustion has a similar inhibitory effect, the MSW fly ash was injected into a coal-fired furnace, doped with HCl.

Results for the coal-fired tests are shown in Figure 6. Even at high HCl levels, coal combustion alone produces negligible PCDD/PCDF. Clearly, the highest S/Cl ratio (1.15), inhibits the formation. This effect is probably not an artifact of the lower HCl concentration: doubling the HCl concentration (1600 to 3200 ppm) for nearly the same S/Cl ratio (0.71 and 0.80), resulted in only a small change in PCDD/PCDF yield. The results MSW fly ash PCDD/PCDF yield for S/Cl = 0.4, however, is inconsistent; highest yields were anticipated under these conditions. The samples are will be re-analyzed to determine if this is due to analysis error. Overall, the coal-fired tests appear to indicate that at S/Cl ratio of 1.15 or above
would result in reduced PCDD/PCDF formation. It should also be noted that after the furnace upgrade, the PCDD/PCDF yields in the IFR are consistently lower. This may be due to better combustion conditions in the burner and higher temperatures, which would tend to destroy some of the organic precursors for PCDD/PCDF formation.

In summary, the pilot-scale IFR results further reaffirm the inhibitory effects of sulfur in PCDD/PCDF formation. While last year's tests have identified S/Cl ratios of 0.7 and 0.8 to be effective for natural gas and coal combustion environments respectively, current tests with a different coal indicate 1.15 to be the effective S/Cl ratio. Also, while results from last year's program have identified the presence of HCl to be a significant parameter, current tests have shown that gas-phase precursor concentration is also important for PCDD/PCDF formation.

Bench-scale results

Bench-scale tests examined the sulfur inhibition mechanisms. Reduced catalytic activity of Cu species due to sulfur is documented (Gullett et al. 1992), but other SO₂ effects have not been researched. The bench-scale tests on the COR tested CuO as the simulated catalytic species on the MSW fly ash. In all the COR tests, the catalyst sample was pretreated for 30 min.

In the first series of tests, the pretreatment was at 400 or 800°C, in an oxidizing atmosphere with or without SO₂. After pretreatment, SO₂ flow was stopped and HCl introduced. The Deacon process (conversion of HCl to presumably Cl₂) was monitored by measuring the outlet HCl concentration, and the responses are shown in Figure 7. It can be seen that the catalytic activity decreases with time, making it necessary to study the transient response for reliable characterization of SO₂ effects. Pretreatment at 400°C with SO₂ had little effect on the Deacon process. XRF and XRD analysis of the sample after the run detected no sulfur or sulfur species. This is surprising since under these conditions CuSO₄ formation was expected. Nevertheless, these results indicate that the effect of sulfur in inhibiting PCDD/PCDF formation may not be due reduced Deacon process activity.

Another possible inhibition effects involves depletion of active chlorine by SO₂. In this work, SO₂ was added to the COR after the catalyst to examine if depletion of the Deacon process product, presumably Cl₂, takes place according to Equation (1) above. The relative magnitudes two inhibition mechanisms, catalyst poisoning and chlorine depletion, were evaluated by comparing between the effects of SO₂ introduced before and after the catalyst plug as shown in the schematic
in Figure 2b.

Results are shown in Figures 8 and 9. All the curves demonstrate that SO\textsubscript{2} offsets the effect of the catalyst, as seen by the higher HCl concentration measured in the presence of SO\textsubscript{2}. It is also seen that SO\textsubscript{2} reacts with the chlorine formed from the Deacon process, as shown by the two post-CuO curves. Figure 9 also shows that the pre-CuO and post-CuO SO\textsubscript{2} effects are nearly the same, suggesting that the inhibition is mostly due to gas-phase depletion with only a small effect of catalyst poisoning. Such a comparison is difficult in Figure 8 due to the large transient in the pre-CuO case in this figure. However, in both cases, it is clear that depletion of chlorine through gas-phase reaction is a mechanism of SO\textsubscript{2} inhibition.

Additional tests were performed in the COR (Figure 2c) to evaluate active chlorine species that can react with SO\textsubscript{2}. While the results discussed above have shown that chlorine species produced from the Deacon process reacts with SO\textsubscript{2} to re-form HCl, it was unclear whether the active chlorine species was molecular chlorine (Cl\textsubscript{2}) or chlorine radicals, present as a reaction intermediate. Therefore, gas-phase reaction studies examined if the reaction

\[ \text{Cl}_2 + \text{SO}_2 + \text{H}_2\text{O} = 2 \text{HCl} + \text{SO}_3 \]

can proceed with molecular chlorine as the reactant. The reaction temperature was increased in steps and the HCl produced was monitored through the HCl monitor. Results are shown in Figure 10. HCl formation is observed as the temperature exceeds 200°C, with the formation increasing with increasing temperature. These results clearly show that molecular chlorine reacts with SO\textsubscript{2} in the presence of moisture. Thus, SO\textsubscript{2} can scavenge the active chlorine present in a process, and its inhibition effect is not limited to the chlorine species produced catalytically through the Deacon process.

Thermodynamic equilibrium calculations were performed using NASA's computer code CET89 for the Cl\textsubscript{2}+SO\textsubscript{2}+H\textsubscript{2}O system. According to these calculations, formation of HCl is also favored thermodynamically, with an increasing trend with temperature. However, presence of SO\textsubscript{2} had no effect on the reaction equilibrium. To verify if this is correct, tests were conducted on the COR where the Cl\textsubscript{2}+SO\textsubscript{2} reaction was allowed to proceed for about three hours, following which SO\textsubscript{2} was replaced with pure N\textsubscript{2}. Results from these tests are shown in Figure 11 for temperatures 400 and 500°C. The decrease in concentration after one hour for the 500°C case may be due to partial condensation of the produced HCl in the gas lines leading to the HCl monitor. Nevertheless, it is evident that
when SO₂ is stopped, the HCl production decreases sharply. Thus, depletion of active chlorine (to form HCl) is driven by reaction with SO₂ and not equilibrium thermodynamics of Cl₂+H₂O system. The disagreement with theoretical calculations may be because, without SO₂, the kinetics of the reaction are too slow.

Previous tests used CuO to represent the catalytic species in the fly ash. Additional COR tests (scheme shown in Figure 2a) involved MSW fly ash (instead of CuO) to determine if the catalytic activity of the fly ash towards the Deacon process is detectable. About 2 g of the MSW fly ash sample was placed in the COR. When the HCl concentration approached the inlet level, the furnace was turned on and the sample heated to 400°C. The sample was held at this temperature for two hours and then cooled by shutting off the furnace. Data for a pair of such runs are shown in Figure 12. There is a large variation between the runs, possibly due to the heterogeneity of the fly ash. However, there is a notable decrease in HCl concentration due to the presence of the fly ash.

Effect of temperature on the above fly ash effect on HCl was examined. The sample temperature was varied in steps and the outlet HCl concentration monitored continuously. Results are shown in Figure 13. For each increase in temperature, the outlet HCl concentration dropped sharply, and then returned to its baseline value; and this behavior occurred over the entire temperature range tested.

It is possible that residual carbon in the MSW fly ash is gasified to produce carbon monoxide (CO) and this CO reacts with HCl. To test this possibility, a fly ash sample was pretreated in air for three hours at 600°C, cooled down to room temperature and then allowed to react with HCl. Again, as shown in Figure 14, there was a significant effect on the HCl concentration. It is therefore unlikely, given the pretreatment conditions, that the fly ash effect on HCl is due to gasification of residual carbon in the fly ash.

Therefore, COR tests with MSW fly ash indicate that the fly ash has a strong affinity towards HCl. This affinity would ensure the availability of HCl at the fly ash surface for the Deacon process to proceed, eventually causing PCDD/PCDF formation.

CONCLUSIONS AND RECOMMENDATIONS

Under both natural-gas and coal combustion conditions, sulfur is effective in inhibiting the formation of PCDD/PCDF. The S/Cl ratio at which the inhibition is effective can vary, and the maximum effective S/Cl ratio necessary is found to be 1.15 in our tests.
Gas-phase precursor concentration is a significant parameter in PCDD/PCDF formation. Therefore, good combustion practices may lower PCDD/PCDF emissions.

Depletion of chlorine through gas-phase reaction is a dominant mechanism of SO₂ inhibition. This inhibition effect is not limited to the chlorine species produced catalytically through the Deacon process.

MSW fly ash exhibits a strong affinity towards HCl at temperatures above 200°C. This would facilitate the access of chlorine species (HCl) to the fly ash surface, leading to eventual PCDD/PCDF formation.

In summary, co-firing municipal waste combustors with coal, when combined with good combustion practices, can lead to reduced PCDD/PCDF formation. The sulfur-to-chlorine ratio in at which effective inhibition takes place can vary, but for the various fuels (natural gas, coals) tested under this project, the maximum necessary is found to be 1.15.

In our research program so far, it has been demonstrated, using simulated MWC conditions in a pilot-scale furnace, that co-firing MWCs with coal can reduce PCDD/PCDF. The next logical step towards establishing that coal-MSW co-firing is commercially viable is to demonstrate the sulfur inhibition effect by actually co-firing MSW with coal.

REFERENCES


Figure 1. Schematic of the Innovative Furnace Reactor (IFR) Facility
Figure 2a. COR scheme for study of SO2 pretreatment

Figure 2b. COR scheme for study of SO2 effects on catalyst poisoning and Cl depletion

Figure 2c. COR scheme for study of Cl2-SO2 reaction
MSW fly ash in natural gas-fired IFR
(no added HCl)

Figure 3. Effect of SO2 without HCl addition
MSW fly ash in natural gas-fired IFR
HCl concentration = 440 ppm

Figure 4. Effect of SO2 injection in gas-fired furnace
MSW fly ash in natural gas-fired IFR
HCl concentration = 440 ppm

Figure 5. Effect of fly ash properties and burn conditions
Figure 6. Effect of coal sulfur in coal-fired furnace
Figure 7. Effect of SO2 pretreatment on Deacon process
Figure 8. Effect of SO2 on overall HCl conversion
Figure 9. Effect of SO2 on overall HCl conversion
Figure 10. Reaction of Cl2 with SO2 at various temperatures
Figure 11. Reaction of Cl2 with SO2 at 400 and 500°C
2 g of MSW fly ash, 1000 ppm inlet HCl

Figure 12. Effect of MSW fly ash on HCl at 400°C
Figure 13. Effect of MSW fly ash on HCl at different temperatures
Figure 14. Effect of MSW fly ash on HCl at 400°C after 600°C pretreatment in air