

THE IMPACT OF CHLORINE ON HEXAVALENT CHROMIUM EMISSIONS FROM A LAMINAR DIFFUSION FLAME

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ABSTRACT

Measurements of total chromium and hexavalent chromium have been obtained in a laminar hydrocarbon/air diffusion flame. Chlorine was added to the fuel as methyl chloride gas. A probe sampled the emissions from the flame. Particles were collected on a filter and vapor phase species were collected in impingers. Hexavalent chromium was measured with a spectrophotometric method. Total chromium added to the flame was determined by gravimetric analysis of the chromium source, chromium hexacarbonyl. The fraction of hexavalent chromium increased significantly as small amounts of chlorine were added. Partitioning between phases was also altered – much more hexavalent chromium was found in the impingers as the chlorine loading increased. Differential mobility analysis of the particles showed that the mean particle size was always in the range of 25-30 nm, whether chlorine was added or not. However, particle concentrations decreased when chlorine was present. Equilibrium calculations showed strong sensitivity to the thermochemical properties of the included species, particularly CrO_2Cl_2 .

KEYWORDS: hexavalent chromium, chlorine, laminar diffusion flame

INTRODUCTION

Metals are often unavoidably introduced into combustion systems. Coal combustion ineluctably introduces metals as part of the mineral matter of the fuel. The incineration of many wastes also suffers a similar problem. Many of these metals can exist in more than one oxidation state, some are of great environmental concern. It is known that the toxicity of the metals is a strong function of the oxidation state. For example, the hexavalent form of chromium is much more toxic than the trivalent form [1, 2]. The physical state of the metal may also depend upon its chemical state, with significant implications for the selection of air pollution control equipment.

The problem of metal transformation and fate is exacerbated in waste incineration when chlorine is present. Many waste streams introduce chlorine as part of the waste itself. The presence of chlorine in the mixture will result in an increase in the emission of vapor phase metals, as the metal chlorides are generally more volatile than the metal oxides. Furthermore, Linak and Wendt [3] showed, via equilibrium calculations, that chlorine has a significant impact on the fraction of the total chromium that appears as hexavalent chromium, primarily through the enhanced formation of the hexavalent CrO_2Cl_2 at a temperature around 700K. This temperature is expected in the post flame gases, and gives rise to the possibility that hexavalent chromium may be formed in the downstream sections of an incinerator if sufficient residence time is available.

A number of earlier studies of the fate of metals in combustion systems have focused on simulations of realistic incinerator conditions [3-5]. Fewer studies have been undertaken in simple flame configurations that are amenable to theoretical or numerical modeling. Premixed flame studies, such as that of Bulewicz and Padley [6], are useful in gaining an understanding of the kinetics of metal oxidation. However, practical combustion systems generally utilize non-premixed reaction. Yoon et al. [7] studied a laminar, hydrogen/air diffusion flame that was seeded with chromium and found that high temperatures favored the formation of hexavalent chromium. They did not add chlorine to the flame.

This paper is an extension of the earlier work of Yoon et al. [7]. It considers the impact of chlorine in a laminar hydrocarbon/air diffusion flame, with particular attention to the issues of speciation of chromium and partitioning between solid and vapor phases. The measurements and equilibrium analysis reveal the impact of varying temperature and oxygen concentration on chromium speciation in the presence of chlorine.

EXPERIMENTAL

The coflow, laminar, diffusion flame system is shown in Fig. 1. The 5 mm burner nozzle was positioned in the center of a 100×100 mm duct containing flow straighteners and a series of fine-mesh screens to ensure air-flow uniformity. Methane (CH_4) was used as the primary fuel in this experiment. A small quantity of CH_3Cl was added into the fuel as a chlorine source. The flow rate of CH_4 was adjusted, according to the CH_3Cl flow rate, so as to keep the mixture flow rate constant. The mole fraction of CH_3Cl in the fuel was in the range from zero to 0.07.

Chromium hexacarbonyl ($\text{Cr}(\text{CO})_6$), a volatile crystal that decomposes at 210 °C to produce elemental Cr, was used as a chromium source in the experiment. A glass cartridge containing chromium hexacarbonyl was added to the fuel delivery line. The $\text{CH}_4/\text{CH}_3\text{Cl}$ mixture flowed through the cartridge at a rate of 0.160 L/min. With temperature controlled at 24 °C, the vapor pressure resulted in a chromium concentration of 60 ppmv. The concentration of chromium in the carrier gas was obtained gravimetrically by comparing the mass difference of chromium hexacarbonyl in the cartridge before and after the experiment. Chromium hexacarbonyl vapor carried in the fuel decomposed quickly in the flame to provide zero-valence chromium.

Samples of vapor and particle phases of chromium compounds emitted from the flame were obtained with a stainless steel sampling probe positioned above the flame on the centerline. The 200-mm-long, 22-mm-outer diameter sampling probe contained a 150-mm-long, 13-mm-inner diameter sintered metal tube as its inner wall. Nitrogen dilution gas was provided to the sampling probe through its inner wall and mixed with the sample to quench reactions, the development of aerosols through the sampling lines, and to minimize the transport of particles and vapors to the probe wall. The flow rate of nitrogen was fixed at 0.8 L/min, accounting for more than 25% of the total sampling flow rate, which was deemed adequate to serve those purposes mentioned above [7].

Figure 2 shows the chromium sampling system. The particle phase of chromium, and some absorbed gas phase material, was captured on a 47-mm-diameter alumina membrane filter with 20 nm pores. The temperature of the filter, and the sampling lines between the probe and the filter, was kept slightly above 100°C by heating with heating tapes, to prevent water condensation along the lines and on the filter, and avoid interconversion between Cr(VI) and Cr(III). All of the samples were obtained above the flame tip at a distance of 55 mm from the nozzle exit where the temperature was 1400 °K on the centerline. The flame tip was approximately 26 mm from the nozzle exit for all the experiments.

The impingers and liquid nitrogen trap were designed to capture the vapor phase of the chromium compounds. A NaHCO_3 solution was used in the impingers to prevent further conversion between Cr(VI) and Cr(III). HCl was a major product of the $\text{CH}_4/\text{CH}_3\text{Cl}$ flame; the pH of the NaHCO_3 buffer solution was adjusted to accommodate the CH_3Cl concentration in the fuel and the resultant concentration of HCl in the sample.

The sampling time for each sample was 1 hour. The filter was cut into two halves, one for hexavalent chromium analysis and another for total chromium analysis. Samples from the impingers and the liquid nitrogen trap were analyzed solely for hexavalent chromium. Sampling lines before the filter were rinsed with deionized water for hexavalent chromium analysis. In the experiments reported herein, there was no measurable amount of hexavalent chromium detected in the samples from the liquid nitrogen trap and those from rinsing the sample lines.

The half filter for Cr(VI) analysis was extracted with a 0.01 N NaHCO_3 solution for 20 hours before the extraction solution was analyzed by a spectrophotometric method as described in EPA Method 7196A [8]. An X-ray fluorescence (XRF) method was used to measure the total chromium on the filter with a Kevex 0700/8000 energy dispersive XRF spectrometer. Total chromium consumed in the experiment was determined from the mass difference of the chromium hexacarbonyl in the cartridge before and after the experiment with a Mettler AJ100 balance.

A TSI Model 3934 SMPS (Scanning Mobility Particle Sizer) system was used for the particle size analysis. A denuder containing sodium hydroxide was added to the sampling line to eliminate H_2O and HCl from the sampled post flame gases. A post flame aerosol stream of 0.6 L/min was fed into the particle size analyzer.

RESULTS AND DISCUSSION

A series of samples were taken at a fixed sampling point 55 mm above the nozzle to study the combustion products with varying chlorine concentrations in the fuel. With the chlorine concentrations that were used in these experiments, the flame length did not show a measurable change. Cr(VI) mass on the filter was compared with the total chromium mass on the filter. As an abbreviation, this fraction is referred to as "on-filter Cr(VI) fraction" hereafter. The total Cr(VI) mass from both the filter and the impingers was compared with the total chromium consumed in the experiment, and this fraction is referred to as "overall Cr(VI) fraction" hereafter. The Cr(VI) emitted in the vapor phase and trapped in the impingers was compared with the total chromium consumed in the experiment. This fraction is referred to as "gas-phase Cr(VI) fraction" later in this paper. Similarly, the Cr(VI) captured on the filter was compared with the total chromium consumed in the experiment, and this fraction was referred to as "solid-phase Cr(VI) fraction" hereafter. The fraction of the total input chromium that was recovered was evaluated by comparing chromium recovered on the filter and in the impingers with the total chromium supplied in the fuel. Without chlorine we found typical recoveries of input chromium

of about 10%. As chlorine was added, the recovery rate increased to up to 64%, as a result of a greater amount of Cr(VI) passing through the filter to the impingers and being detected by the spectrophotometric method.

Figure 3 shows the overall Cr(VI) fraction of the total chromium added to the flame; it is plotted against varying CH₃Cl concentrations in the fuel. Since it was possible that some of the flame emission was not collected into the sampling probe, this fraction can be interpreted as a lower limit of the Cr(VI) fraction. Nevertheless, the samples showed a clear increase in Cr(VI) with increasing CH₃Cl concentration in the fuel. This trend is consistent with measurements in practical systems. Volland [9] reported results from a variety of tests on medical waste incinerators in which stainless steel "sharps" may provide a significant source of chromium. Without chlorine in the feed, about 16% of the stack gas chromium appeared in its hexavalent state. With 8.5% chlorine in the feed, the fraction of hexavalent chromium increased to about 48%. Our results confirm the strong impact of chlorine on the propensity to form hexavalent chromium.

It was also found that the on-filter Cr(VI) fraction increased to 1 as only a small amount of chlorine was added, while the typical value for samples from experiments without chlorine was around 0.2, as illustrated in Figure 4. The increase in the on-filter hexavalent fraction was accompanied by a change in the color of the filter. Without chlorine, the filters were reddish-brown, suggestive of CrO₃. As chlorine was added, the filters changed color to green and further yielded a light green solution when extracted with water. We expect, from equilibrium calculations discussed later, and from its solubility, that the compound CrO₂Cl₂ may be responsible for the observed color change.

The presence of chlorine affects not only the chemical state of the metal, but also its physical state, largely as a result of the formation of more volatile metal chlorides that tend to yield gas phase products. Sampling at the same point above the flame showed that gas-phase Cr(VI) increased with increasing concentration of chlorine in the fuel, while the solid-phase Cr(VI) fraction remained at a steady level for all the chlorine concentrations, as shown in Figure 5. This trend is in agreement with observations from practical incinerators [9].

Differential mobility particle analysis showed some impact of chlorine on the particle size distribution in the post flame gases. While the mean particle size was always found to be in the range of 25-30 nm, not very sensitive to CH₃Cl concentration in the fuel, a decrease by a factor of 10 was observed in particle concentration when CH₃Cl concentration in the fuel increased to about 0.03. This is in agreement with the increase in gas-phase Cr(VI) associated with increasing CH₃Cl concentration in the fuel.

An equilibrium calculation considered the following species: CH₃Cl, CH₄, CO, CO₂, Cl₂, Cr, CrOCl₂, CrOH₃, CrOOH, CrO₂, CrO₂Cl, CrO₂OH, CrO₂(OH)₂, CrO₃, Cr₂O_{3(s)}, HCl, H₂O, N₂, and O₂. This list is by no means an exhaustive compilation of all possible species. As Linak and Wendt [3] and Kashireninov and Fontijn [10] pointed out, equilibrium calculations can be affected dramatically by the choice of species that are included. Nevertheless, the important species that were identified by these authors were included in the calculation. In addition to the impact of the choice of species, we have found that uncertainties in the thermochemical data, in particular that for the species CrO₂Cl₂, can be important. The enthalpy of formation for CrO₂Cl₂ reported by Ebbinghaus [12] was -519.2 kJ/mol, slightly higher than that reported by Barin [11] of -538.062 kJ/mol. Calculation showed that with these different values of enthalpy of formation, the equilibrium concentration of CrO₂Cl₂ could vary by a factor of 10. We have chosen to use the heat of formation for CrO₂Cl₂ that was reported by Barin. The results of a STANJAN calculation are presented in Fig. 6 in which Cr₂O₃ was considered to be in its solid form. The temperature was found from imposing an adiabatic condition.

The predicted equilibrium fraction of hexavalent chromium exhibits a maximum at a temperature of about 1400 °K. In contrast, Kashireninov and Fontijn [10] found a *maximum* in the Cr(VI) fraction at a temperature of about 1600 °K. Furthermore, these authors found that CrO₂Cl₂ was not significant down to temperatures of 1000 °K. Wu and Biswas [13] reported equilibrium results for the CH₄-air-Cl₂ system at temperatures of 1100 °K and 1500 °K. They used a combination of data from Barin [11] and Ebbinghaus [12]. The equilibrium results showed that CrO₂Cl₂ was not significant until temperatures dropped below 1000 °K. At higher temperatures, CrO₂(OH)₂ was the dominant hexavalent species. On the other hand, Linak and Wendt [3] showed that CrO₂Cl₂ was an important species in equilibrium over a broad range of temperatures from 500 °K to 1500 °K. The importance of CrO₂Cl₂ is apparent in Fig. 6. It is the dominant hexavalent chromium species in very lean mixtures and, of course, only appears when chlorine is present. In richer mixtures at concomitantly higher temperatures, chlorine makes little difference in the equilibrium fraction of hexavalent chromium.

The relevance of the equilibrium predictions to the measurement that we have undertaken can be understood if the equilibrium concentrations are plotted as a function of temperature and equivalence ratio. The equivalence ratio was obtained from thermocouple temperature

measurements. It was assumed that heat-releasing chemical reactions were complete at the measurement locations in the post flame gases. An adiabatic mixing calculation was performed to find the number of moles of air that were required to mix with combustion products to achieve the measured temperature. Equilibrium calculations were then run for the measured temperature and estimated equivalence ratio as a function of radial location. The temperature profile and the equilibrium mole fractions are shown in Fig. 7. It should be recalled that the sampling probe drew in most of the post flame gases. The measured hexavalent chromium fraction on the filter and in the impingers arises from streamlines that have passed through both the centerline of the flow and through peripheral regions. Temperatures and equivalence ratios in the latter regions are lower than along the centerline. The increase in Cr(VI) with chlorine addition can be understood in terms of an increase in CrO_2Cl_2 at the cooler edges of the flow. Equilibrium calculations suggest that Cl addition should have little impact on Cr speciation in the hotter gases on the centerline of the flow. The change in color of the filter with chlorine addition is consistent with this structure of the flow.

CONCLUSIONS

Chromium sampling in a $\text{CH}_4/\text{CH}_3\text{Cl}$ flame has been performed using an N_2 dilution sampling probe, an alumina membrane filter, two impingers and a liquid nitrogen trap. All the samples were analyzed by EPA Method 7196A and X-ray fluorescence spectrometry to quantify the amounts of Cr(VI), and the partitioning of Cr(VI) phases. Flame products were analyzed with a TSI Model 3934 SMPS particle size analyzer. The results of Cr sample analysis showed a significant Cr(VI) fraction increase in the post flame gases with increasing concentration of CH_3Cl in the fuel. The fraction of Cr(VI) emitted as vapor increased with increasing CH_3Cl concentration in the fuel. It was also found that the color of the sample on the filter changed from dark brown to light yellow-green as CH_3Cl concentration in the fuel increased, which suggested there was a change in the species distribution among the combustion products. This change was attributed to the increased presence of CrO_2Cl_2 in the post flame gases. Particle size analysis showed that the particle concentration in post flame gases decreased with increasing CH_3Cl concentration in the fuel, while no significant change was found in the mean particle diameter as CH_3Cl concentration in the fuel varied. Equilibrium calculations agreed with the observed Cr(VI) fraction change with varying CH_3Cl concentration if the enhanced Cr(VI) yield is ascribed to enhanced CrO_2Cl_2 formation on the edge of the jet. The equilibrium results showed some sensitivity to the choice of thermochemical properties of CrO_2Cl_2 .

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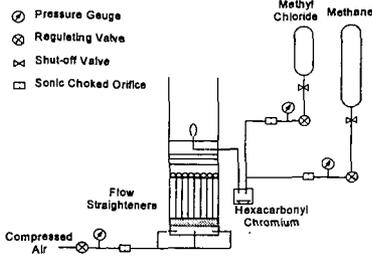


Figure 1 Schematic of experimental apparatus

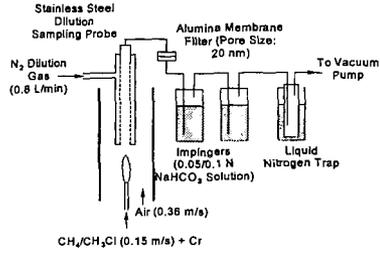


Figure 2 Schematic of chromium sampling system

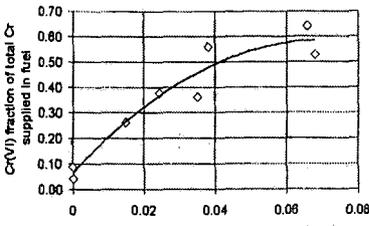


Figure 3 Cr(VI) Fraction of Total Cr Supplied in Fuel vs. CH3Cl Concentration in Fuel

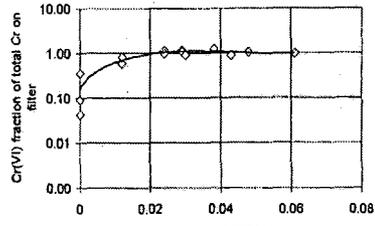


Figure 4 Cr(VI) Fraction of Total Cr on Filter vs. CH3Cl Concentration in Fuel

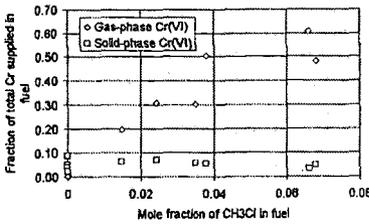


Figure 5 Gas-phase and Solid-phase Cr(VI) Fraction of Total Cr Supplied in Fuel vs. CH3Cl Concentration in Fuel

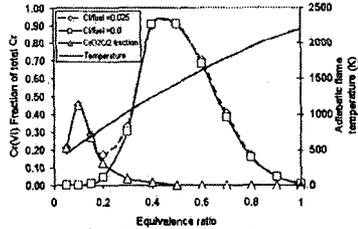


Figure 6 Adiabatic Equilibrium Temperature, Total Cr(VI) Fraction, and Fraction of Total Cr as CrO2Cl2 vs. Equivalence ratio

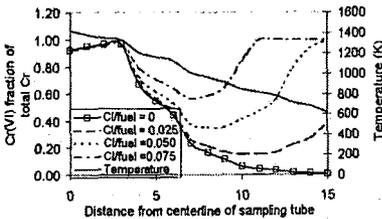


Figure 7 Measured Temperature Profile across Flame at Sampling Location and Calculated Equilibrium Cr(VI) Fraction of Total Cr