

Fourth International Conference on
Technologies and Combustion for a Clean Environment
July 7-10, 1997
Lisboa, Portugal

Metal Partitioning in Combustion Processes

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Abstract -- This article summarizes ongoing research efforts at the National Risk Management Research Laboratory of the U.S. Environmental Protection Agency examining (high temperature) metal behavior within combustion environments. The partitioning of non-volatile (Cr and Ni), semi-volatile (Cd and Pb), and volatile (Hg) metals in combustion systems was investigated theoretically and experimentally. Theoretical predictions were based on chemical equilibrium and suggested that such calculations can be useful in predicting relative volatility and speciation trends, and to direct experimental efforts. Equilibrium calculations, however, are not sufficient to quantitatively predict the behavior of metals even in simple combustion environments. Experimental studies employing a 59 kW laboratory scale combustor examined the behavior (volatility, particle size, and speciation) of metal vapors and particles produced by aqueous metal solutions sprayed through a swirling natural gas diffusion flame. These experiments were designed to study metal transformation mechanisms in a relatively simple combustion environment without the complex effects of additional species. Further experiments examined the potential use of common inorganic sorbents (kaolinite, bauxite, and hydrated lime) to adsorb metal vapor, offering a potential means of metal emissions control.

Key Words: Trace Metals; Partitioning; Volatility; Sorbent Interactions; Combustion

INTRODUCTION

Metal compounds are present in the stack effluents of many combustion processes. As health and environmental studies further identify the scope and magnitude of their adverse effects, the release of metals from boilers, furnaces, and incinerators into the environment is coming under increasing regulatory scrutiny in a number of countries. In the U.S., metal air emissions from hazardous waste incinerators (HWIs) and boilers and industrial furnaces (BIFs) which destroy hazardous waste are regulated by the Resource Conservation and Recovery Act (RCRA, 1986). Current air emission limits are based on risk assessment arguments which limit the ground level concentrations that may be inhaled by the "maximum exposed individual." Metals regulated by RCRA include a set of carcinogenic metals [arsenic (As), beryllium (Be), cadmium (Cd), and chromium (Cr)] and a set of noncarcinogenic metals [antimony (Sb), barium (Ba), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), and thallium (Tl)]. Metal air emissions from many other combustion sources are regulated under Title III, Section 112 of the Clean Air Act Amendments (CAAA, 1990). Metals regulated by Section 112 include Sb, As, Be, Cd, Cr, cobalt (Co), Pb, manganese (Mn), Hg, Ni, and Se. While municipal waste incinerators (MWIs) are also regulated under Title III, these units are covered by their own set of metal emission regulations (Section 129), which are likely to place limits on the emissions of Cd, Pb, and Hg.

This paper, which presents results from theoretical and experimental studies conducted by EPA's National Risk Management Research Laboratory, is concerned with the partitioning of metals in combustion processes. Under well defined conditions, metals can be segregated according to their relative volatilities. Rizeq *et al.* (1994) group metals into three volatility classes. Metals, such as Hg and Se, tend to be volatile, even at moderate stack temperatures. Others, such as Sb, As, Cd, Pb, and Tl, are semi-volatile, and have the potential of vaporizing at the high temperatures in the flame zone. Finally, a third group including Ba, Be, Cr, and Ni, are considered to be refractory (non-volatile) over the entire range of combustion temperatures usually encountered. Of interest are the physical and chemical transformations from the initial form of the metal to

its speciation and partitioning between the submicron (<1 μm in diameter) and supermicron (>1 μm in diameter) aerosol in the exhaust. Of particular interest are methods of affecting metal speciation and particle size to maximize control and minimize toxicity and risk.

While much previous research on mechanisms governing the transformations of metal compounds in combustion systems has focused on coal combustion systems (Flagan and Friedlander, 1978; Nettleton, 1979; Smith, 1980; Haynes *et al.*, 1982; Neville and Sarofim, 1982), relatively little is available on the fate of single metal compounds, introduced one at a time, in the absence of other major ash constituents, as they might be during incineration trial burns. The coal data suggest that trace metals are often enriched in the submicron particle size fraction, and this has been explained by mechanisms involving metal vaporization and subsequent condensation or surface reaction. There are complicated exceptions, including cases where a volatile metal, such as sodium (Na), may be scavenged by aluminosilicates displacing other bound metals. Therefore, experiments involving relatively simple combustion environments and pure metal compounds (such as those presented here) are useful to test theoretical hypotheses and help isolate mechanisms.

Mechanism Overview

Metals may be contained in solid or liquid fuels, chemically bound to the organic fuel matrix (inherent mineral matter), dispersed within the solid fuel as mineral crystallites (included mineral matter), or completely extraneous to the fuel particle (excluded mineral matter). Metals may be chemically bound within organometallic compounds such as chelates or physically mixed, as in paints, pigments, and solvents. They may enter combustion processes with other inorganic clays and soils, as during the thermal treatment of contaminated soils (Eddings and Lighty, 1992), or they may be contained in aqueous solutions and sludges. Metals may be introduced into a combustion environment continuously through atomizers (Bhatia and Sirignano, 1991), lances, or screw feeders, or through entrance chutes in a batch mode as solids or contained liquids. They may be introduced as single salts or individual compounds, or they may enter as mixtures. In fact, a critical issue in designing test burns for incinerators is whether the form in which the metal is introduced during the trial burn is representative of the behavior of other forms of that metal that may be introduced during routine operation. The left-hand side of Figure 1 represents some of the various forms in which a metal may be introduced into a combustor, and how this physical state can influence the ultimate fate of that metal.

Upon entry into a combustion environment, the metals contained in a fuel or waste stream can be transformed into various physical forms. Dissolved metal salts, such as nitrates or pyrites, may form reactive metal compounds which may decompose violently at elevated temperatures. They may also decompose as viscous melts to form cenospheres which can burst into submicron fragments (Mulholland and Sarofim, 1991). Alternatively, the metal compound may be confined within a porous char matrix. This will happen, for example, to inherent (organically bound) metals in heavy oil or both inherent and included mineral matter in pulverized coal. The metal must then be released either within the matrix, subsequently to diffuse through it, or it will enter the gas phase as the char matrix itself is oxidized. In the event of the former process, there is the opportunity for the metal to react with included silicates to form stable compounds which fail to vaporize. Alternatively, the metal which has been released may diffuse back into the remaining char matrix, to react with included silicates situated there, or it may react with excluded silicate particles in the disperse phase. Finally, one metal (e.g., Na) may displace another metal [e.g., potassium (K)] which would otherwise be immobile and bound in a stable mineral

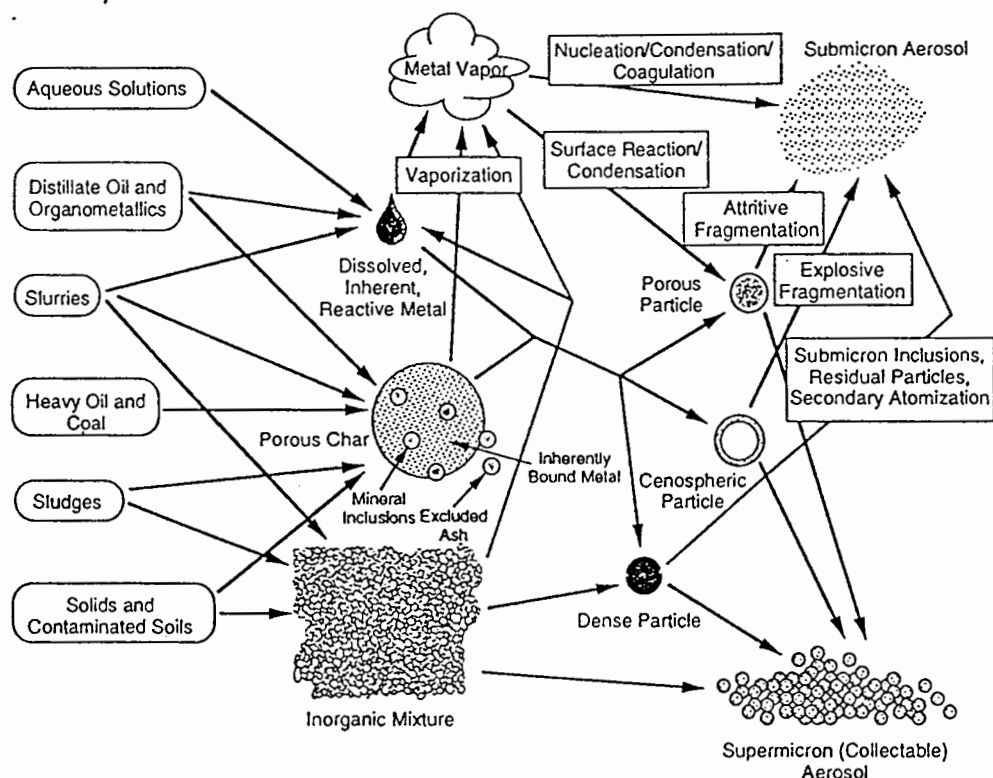


FIGURE 1 Possible controlling mechanisms for particle formation in combustion systems.

form, such as illite. Mineral inclusions may also coalesce as the carbon matrix recedes to form particles larger than the individual inclusions. The physicochemical processes involved in the release of metals may thus be quite complex. They may be kinetically controlled, and the overall amount of a metal released may, under certain circumstances, have little to do with equilibrium.

When a metal contained in contaminated soils, sludges, or slurries is introduced into an incineration environment, an inorganic mixture containing both the metal and potential scavenging agents, such as clays and glasses, is formed. It is not surprising, therefore, that (upon heating) much of the metal may react with the clay and only a little will be released to form a condensable vapor. This has been experimentally confirmed for Pb/montmorillonite clay mixtures by Eddings and Lighty (1992). Their study showed large deviations from simple equilibria based on selected pure condensed phases, during the heating of inorganic mixtures. The work of Queneau *et al.* (1991) addresses the thermodynamics of the vitrified mixtures likely to be formed under these conditions, and is useful where inorganic mixtures are formed, as shown in Figure 1.

The primary physical forms of the metals outlined above (reactive metal compounds, porous chars, and inorganic mixtures as shown in Figure 1) can then undergo further transformations to other physical forms including metal vapors, porous metal ash particles, cenospheric (hollow) ash particles, or dense ash particles. Upon cooling, the supersaturated vapor may condense on the surfaces of existing particles, or if sufficient surface area is not available, homogeneously nucleate to form tiny particles. These particles will subsequently collide, coagulate, and agglomerate. Alternatively, there is evidence that a metal vapor may react on the surface of existing particles or sorbents. In contrast to the first two processes (heterogeneous condensation and homogeneous nucleation), surface reaction does not require the metals' partial pressures to exceed their vapor pressures. These mechanisms and processes strongly influence the chemical and physical form in which the metal under consideration enters the environment. They are likely to depend strongly on the combustion environment and temperature history experienced by the metal compound, as well as on the initial form in which it is introduced into the combustion chamber, and on the presence or absence of other species in the mixture.

Particle Growth via Coagulation

In addition to the heterogeneous condensation of vapor-phase species, particle growth occurs through particle coagulation and agglomeration. Figure 2 illustrates the predicted evolution of an aerosol due to coagulation only. The MAEROS code (Gelbard and Seinfeld, 1980) was used in which the particle size domain [0.001 to 20.0 μm particle diameter (D_p)] was divided into 13 geometrically equal sections or bins. Coagulation was the only mechanism considered; all other mechanisms (condensation, nucleation, deposition, etc.) were disabled. At time zero, an initial mass of 500 mg/m^3 was assigned to section 2 (0.0021 - 0.0046 μm diameter) to

simulate the nucleation of a submicron fume. This aerosol was assumed to have the properties of Pb-oxide, producing a number concentration of $4.0 \times 10^{18}/\text{m}^3$. An additional 500 mg/m^3 of mass was assigned to section 11 (2.0-4.4 μm diameter) to simulate the presence of flyash or sorbent. System pressure and temperature were maintained at 1.01×10^5 Pa (1 atm) and 810 K (1000 $^\circ\text{F}$) to simulate post-flame conditions. Following the initial distribution, Figure 2 presents six mass distributions which follow the evolving aerosol through six orders in time ($t=0.1, 1.0, 10, 100, 1000, 10000$ s). Note that coagulation does not change the total aerosol mass and that the areas under all seven curves represent 1000 mg/m^3 . Number concentrations, however, are greatly affected, and Figure 2 shows that at 0.1 s the number concentration has fallen approximately 2 orders of magnitude ($2.3 \times 10^{16}/\text{m}^3$), and the average nuclei size has grown to approximately 0.03 μm . At 1.0 and 10.0 s the distributions have grown only slightly farther into the 0.01 to 1.0 μm diameter range. This is important, as these times represent a range of typical residence times within combustion/incineration systems. In fact, even after 10000 s (2.8 hours) the average D_p is only approximately 1.0 μm with a number concentration of $3.3 \times 10^{11}/\text{m}^3$. Thus, as can be seen from Figure 2, aerosol nuclei tend to coagulate very quickly at small times, due to the large number concentrations of nuclei particles, and then, at larger times, as number concentrations fall, coagulation slows considerably causing the aerosol to accumulate into a mode approximately between 0.1 and 1.0 μm diameter. Particles in this size range, possessing neither high diffusivities nor high momentum, exhibit minimum collection efficiencies in most air pollution control devices. This characteristic distribution of a coagulating aerosol has been termed the accumulation mode. Note that the coagulation mechanism does not include the effect of differing fractal properties of the agglomerate formed, as developed by Matsoukas and Friedlander (1991). It has been assumed here that only spheres result from the coagulation process.

Also evident from Figure 2 is that coagulation between the evolving nuclei and the sorbent is very slow, and the small particles grow as if the sorbent were not present. Again, this is due in part to the large differences in number concentrations. At time zero, nuclei are present in concentrations of approximately $4.0 \times 10^{18}/\text{m}^3$. Sorbent particles are present in concentrations of $4.7 \times 10^9/\text{m}^3$. This difference encourages nuclei-nuclei coagulation. Thus, it would seem that the use of a sorbent to scavenge submicron metal particles through coagulation is not possible in the times available. However, as has been described previously, mechanisms other than coagulation may allow sorbents to be utilized to remove aerosol mass from the submicron fraction. Again, these results assume a fractal dimension of 3 (i.e., spheres) for the resulting agglomerates. Even though the simulation presented in Figure 2 shows very little nuclei-sorbent interaction, fine particle coagulation and diffusion to the coarse mode are competitive processes. Friedlander *et al.* (1991) reason that, since diffusion and coagulation are first and second order with respect to particle number concentration, respectively, one should expect the following qualitative behavior. If, as presented in Figure 2, particle nucleation results in a large initial number concentration, then coagulation will dominate, causing the

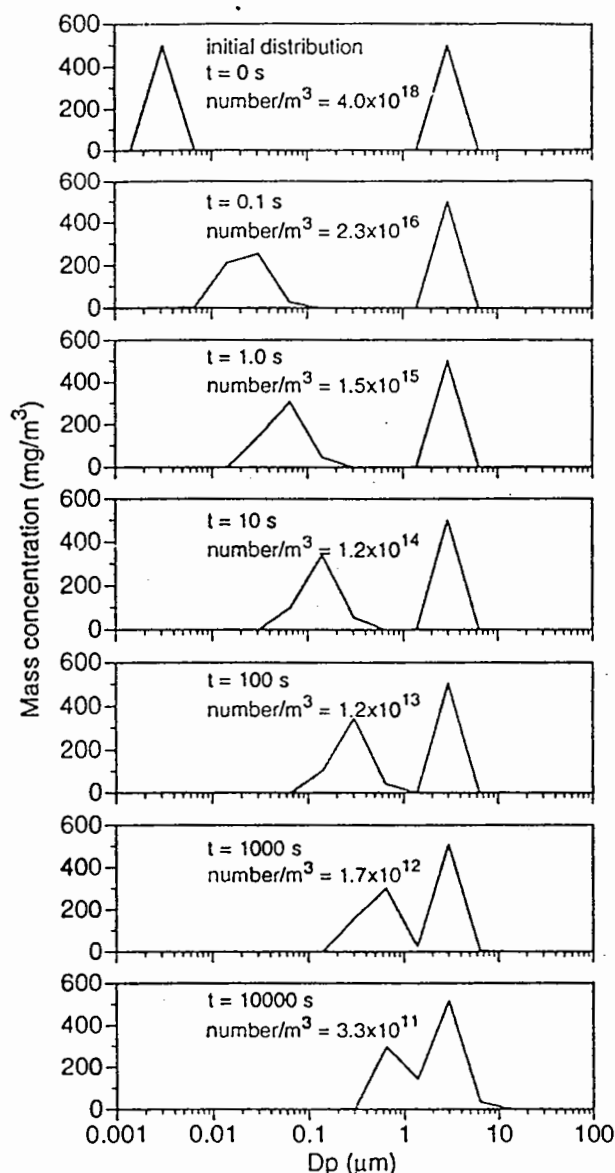


FIGURE 2 Predicted evolution of Pb-oxide nuclei particles in the presence of a simulated sorbent via coagulation in a post-flame combustion environment.

nuclei to grow into particles with low diffusivities and little possibility to be scavenged by the coarse mode particles. If, on the other hand, nucleation results in a small initial nuclei number concentration, nuclei-nuclei coagulation rates will be small, the nuclei mode will not grow substantially but, provided sufficient residence time is available, will diffuse to, and be scavenged by, the coarse mode particles. Thus, using the self preserving size distribution theory, Friedlander *et al.* (1991) argue that significant scavenging of nuclei by coarse mode (sorbent) particles is possible if: the diffusion time [see Flagan and Friedlander, (1978); Friedlander *et al.*, (1991)] is small compared to the residence time; and the mass of the fine mode is below a threshold value for a given coarse mode aerosol.

EXPERIMENTAL APPROACH AND PROCEDURE

Laboratory Swirl Flame Combustor

Experiments were performed using the laboratory scale 59 kW (actual), 82 kW (maximum rated) horizontal tunnel combustor presented in Figure 3. This refractory-lined research combustor was designed to simulate the time/temperature and mixing characteristics of practical industrial liquid and gas combustion systems. Natural gas fuel, aqueous metal solutions, gas dopants, and combustion air were introduced into the burner section through an International Flame Research Foundation (IFRF) moveable-block variable-air swirl burner. This burner incorporates an interchangeable injector positioned along its center axis. Swirling air passes through the annulus around the fuel injector promoting flame stability and attachment to the water-cooled quarl. A high swirl (IFRF type 2) flame with internal

recirculation (Swirl No.=1.48) was used. Gaseous and aerosol samples were taken from a stack location 5.9 m from the burner quarl. The temperature at this location was approximately 670 K (745 °F). Further details regarding the experimental combustor can be found elsewhere (Linak *et al.*, 1994, 1995, 1996, 1997).

Metal Systems Investigated

To date, experimental investigations examining four metals (Cd, Cr, Pb, and Ni) have been conducted and published (Linak *et al.*, 1994, 1995, 1996, 1997). Additional studies focusing on Hg, vanadium (V), and zinc (Zn) are on-going. Typically, water soluble metal nitrates or oxides were introduced as aqueous solutions through a special fuel/waste injector which incorporated a small air atomizing system down the center of a standard natural gas injector. The resulting droplet size distribution was relatively narrow with a mean droplet diameter of approximately 50-80 μm (Linak *et al.*, 1994). Diatomic chlorine (Cl₂) or sulfur dioxide (SO₂) dopants were introduced, separately from the metal solutions, with the (secondary) combustion air. Thus, the metal and chlorine or sulfur, were not mixed prior to their introduction into the combustor. All interactions between the components were dependent upon normal turbulent mixing patterns.

Aqueous solutions typically containing 1.5% metal (by weight) were used. Solution flow rates were maintained so as to produce stack gas concentrations of approximately 100 ppm metal (by volume). Metal feed rates corresponded to constant molar feed rates of approximately 0.005 g-moles/min. Experimental programs included evaluating the effects of chlorine and sulfur on metal partitioning. For these experiments, Cl₂ or SO₂ were introduced at different molar ratios of chlorine or sulfur to metal. These feed rates and resulting stack concentrations varied from substoichiometric with respect to the metal concentration to excess concentrations approaching 10,000 ppm (stack). Typically, chlorine and sulfur stack concentrations of 1000 ppm were examined. Excess air was maintained at 20%. No air preheat was employed.

Aerosol Particle Size Distribution: Sampling and Analysis

Particle size distribution (PSD) measurements were taken from the stack location using three techniques. Extractive samples were taken for collection by inertial impaction and electrical mobility analyses using an isokinetic aerosol sampling system based on the modified designs of Scotto *et al.* (1992) and Linak *et al.* (1994). In order to minimize in-probe gas and aerosol kinetics, the sampling system dilutes and cools the aerosol sample using filtered nitrogen and air immediately after sampling. Dilution ratios are measured directly for each experiment and verified independently by the measurement of a nitric oxide tracer gas.

Extracted samples were directed to an Andersen Inc. eight-stage, 28.3 L/min. (1 ft³/min.), atmospheric pressure cascade impactor and a Thermo-Systems Inc. scanning mobility particle sizer (SMPS). The cascade impactor is designed to collect physical samples less than approximately 10 μm diameter (for subsequent gravimetric and/or chemical analysis) on nine stages (including the after filter). The SMPS classifies and counts particles within a working range of 0.01 to 1.0 μm diameter using principles of charged particle mobility through an electric field. The SMPS, used for later experiments, is an upgraded version of the differential mobility particle sizer (DMPS), used during early experiments. The SMPS upgrade allows for improved PSD resolution and shorter sampling times. The SMPS and DMPS were configured to yield 54 and 27 channels, respectively, evenly spaced (logarithmically) over the 0.01 to 1.0 μm diameter range.

In addition to the inertial impaction and electrical mobility devices which require an extracted sample, *in-situ* light scattering PSDs were taken using an Insitex Inc. laser doppler velocimeter. This instrument determines particle size by measuring the light scattering intensity of particles which pass through a sampling volume established within the combustor stack by a laser focused through a set of quartz optical access ports. The working range of this device was approximately 0.3 to 30 μm diameter which slightly overlapped and extended the PSD data collected by the SMPS.

In addition to the three PSD instruments, samples were collected on silver filters and analyzed using a field emission scanning electron microscope (SEM) equipped with an energy dispersive x-ray (EDX) spectrometer. This provided morphological information as well as qualitative chemical analysis of individual particles.

NON-VOLATILE METALS

Volatile and semi-volatile metals have been of particular interest because they remain as vapors within combustion and flue gas cleaning systems, resulting in poor removal efficiencies, or tend to form fumes of submicron particles resulting from nucleation and condensation of metal vapor. These mechanisms lead to substantial enrichment of these metals on submicron particles which are often difficult to collect in particulate pollution control equipment. It has been shown (Scotto *et al.*, 1992; Wendt, 1994; Linak *et al.*, 1995) that some metal vapors can also be reacted at high temperatures above their dewpoints with sorbent substrates to form environmentally benign water insoluble products. Thus, the emissions of some of these volatile and semi-volatile metals can be managed because they form a vapor which can be scavenged and reacted. However, several researchers

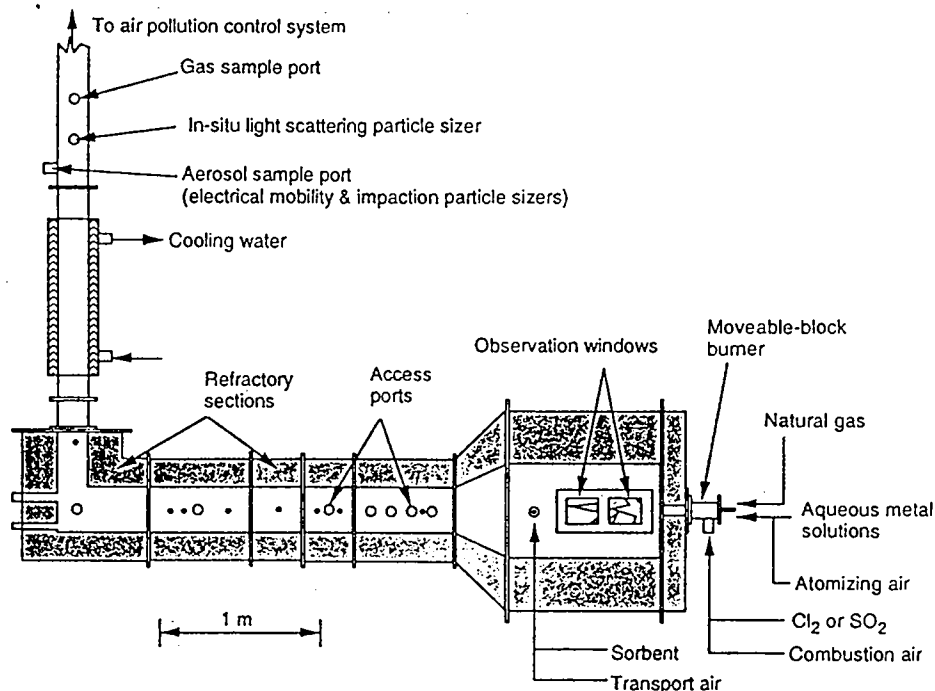


FIGURE 3 EPA horizontal tunnel combustor.

(Davison *et al.*, 1974; Klein *et al.*, 1975; Markowski *et al.*, 1980; Quann and Sarofim, 1982) have also noted enrichment of the refractory metals Ni and Cr in submicron particles, even though it is not obvious that these metals necessarily vaporize in the combustion process. The mechanisms by which this occurs are not readily apparent. It is appropriate, therefore, to examine refractory metals, and to determine if their partitioning among various particle sizes can be predicted and controlled.

Among possible refractory metals we focused on Ni and Cr. Ni is only slightly less volatile than Cr, and appears in both oil and coal flyash. Ni and Cr (metal) have boiling points of 3003 and 2945 K, respectively. Cr is of particular interest because it commonly exists in two forms in the environment (Goyer, 1991; Seigneur and Constantinou, 1995), as either trivalent Cr(III) or hexavalent Cr(VI), as in the chromate anion CrO_4^{2-} (VI) or the compound CrO_3 (VI). Cr(VI) has the lowest risk specific dose for all carcinogenic metals ($0.00083 \mu\text{g}/\text{m}^3$) (Fed. Reg., 1991), while Cr(III) is not considered particularly hazardous. However, from a regulatory viewpoint, all Cr must be considered to be Cr(VI) unless difficult site specific speciation is performed. Therefore, it is important to determine not only how Cr is chemically partitioned among valency states in the exhaust, but also on how this can be manipulated through the addition of sulfur and chlorine compounds, and how the physical partitioning of Cr among various particle sizes occurs in a practical combustion configuration.

Equilibrium Predictions

Multicomponent equilibrium calculations can provide insight into which species are thermodynamically stable at flame and flue gas temperatures. However, the accuracy of equilibrium results depends on the accuracy of the thermodynamic data available, and on the availability of thermodynamic data for all important species containing the elements in question. In addition, equilibrium calculations do not take into account kinetic or mixing limitations and, therefore, represent an idealized solution that may not be realized in practical systems. Thermochemical predictions were determined using the CET89 computer code for calculating complex chemical equilibrium compositions (Gordon and McBride, 1986). Twenty-six Ni species and physical states and 48 Cr species and physical states are considered in these calculations (see Linak *et al.* 1996, 1997). Of interest is the thermodynamic partitioning between vapor and condensed phases, as well as the partitioning between various species. Also, of special interest for Cr is the partitioning between Cr(VI) and other Cr valent species. For both Ni and Cr, the influences of chlorine, sulfur, and both chlorine and sulfur were investigated.

Equilibrium predictions (Figure 4a) indicate that both metals are refractory, with dewpoints of 2000 and 1900 K for 100 ppm Ni and Cr, respectively. Sulfur addition (Figure 4b) has little effect on either metals' dewpoint. Chlorine addition (Figure 4c) lowers the Ni dewpoint by approximately 200 K and moves the Ni curve from the right to the left of the Cr curve, which shows no significant effect of chlorine. The fact that chlorine is more likely to devolatilize Ni than Cr, at high temperatures, suggests that, in the presence of chlorine, high temperature sorbents might be able to capture Ni, but are less likely to capture Cr.

At low temperatures, Ni and chlorine are predicted to form a condensed Ni-chloride salt, thus rendering the residue water soluble. However, chlorine's predicted effect on Cr at low temperatures is profound. Not only is Cr predicted to form vapor-phase Cr-chlorides, but it is also predicted to form the hexavalent Cr-chlorides, CrOCl_4 (VI) and CrCl_6 (VI), as shown on Figure 4c. The presence of sulfur (Figure 4d) completely eliminates the chlorine enhanced formation of low temperature Cr(VI) species, but has

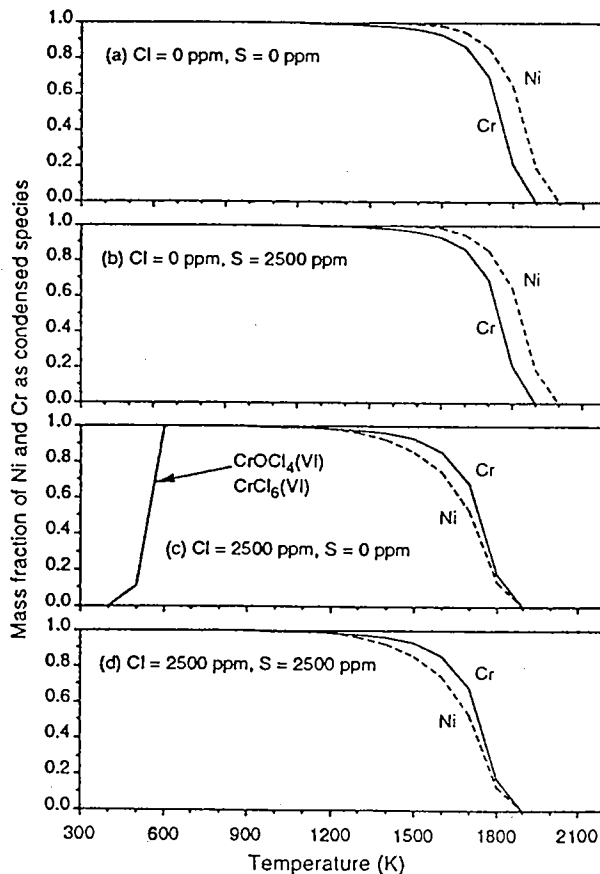


FIGURE 4 Ni and Cr equilibrium predictions for four conditions: (a) 0 ppm chlorine, 0 ppm sulfur; (b) 0 ppm chlorine, 2500 ppm sulfur; (c) 2500 ppm chlorine, 0 ppm sulfur; and (d) 2500 ppm chlorine, 2500 ppm sulfur.

little effect on the high temperature Cr(VI) species (not shown on Figure 4, see Linak *et al.*, 1996). This is because sulfur ties up Cr to form trivalent Cr-sulfate, but only at low temperatures.

The effect of sulfur on the Ni/chlorine mixture is predictable. It has no effect at high temperatures on the devolatilization of Ni, since Ni-sulfates are unstable there, while its effect at low temperatures is merely to replace a solid Ni-chloride by a solid Ni-sulfate. Additional calculations exploring the equilibrium effects of calcium addition showed that calcium, even at concentrations in excess with respect to sulfur, displaced neither the Ni- nor the Cr-sulfate and, therefore, had no appreciable effect on Ni or Cr partitioning.

Particle Size Distributions without Chlorine

Figure 5 presents the PSDs for Ni [injected as $\text{Ni}(\text{NO}_3)_2$], for Cr(III) [injected as $\text{Cr}(\text{NO}_3)_3(\text{III})$], and for Cr(VI) [injected as $\text{CrO}_3(\text{VI})$]. These data (open symbols) were obtained using the SMPS for particles in the 0.01 to 1.0 μm diameter size range and the *in-situ* light scattering particle sizer for particles the 0.3 to $>10 \mu\text{m}$ diameter size range. Each panel also shows the effect of chlorine addition (solid symbols), where the chlorine was added as Cl_2 gas, with the secondary combustion air. While complementary impactor samples were taken, those data are not presented here but may be found elsewhere (Linak *et al.*, 1997).

It should be noted that all three methods of particle collection and sizing produced consistent results that supported each other. Data from the *in-situ* light scattering particle sizer slightly overlapped and extended the range of the SMPS for the sampled particles. This suggests that the isokinetic dilution sampling procedure used maintained aerosol size integrity.

The Ni volume PSD without chlorine (Figure 5a) showed a maximum at about 0.3 to 0.4 μm diameter. For Cr(III) without chlorine, a single particle size mode peaking between 1.0 and 10 μm diameter is shown by both the *in-situ* light scattering particle sizer data (Figure 5b) and the impactor data (data not shown, see Linak *et al.*, 1997). For Cr(VI), two modes are apparent from the SMPS and the *in-situ* light scattering particle sizer, with a dominant mode peaking at about 0.1 to 0.3 μm diameter (Figure 5c). This is verified by the impactor results (data not shown), which also show a dominant mode at about 0.2 to 0.3 μm diameter. These results suggest that $\text{CrO}_3(\text{VI})$ vaporized, while $\text{Cr}(\text{NO}_3)_3(\text{III})$ did not. The difference in volatilization behavior of the two Cr compounds is, of course, in contrast to

equilibrium predictions, which are independent of the initial Cr speciation.

Effect of Chlorine

Chlorine has a significant effect on the Ni number and volume PSDs. The maximum number concentration now occurs at 0.03 μm diameter (data not shown), while the maximum volume concentration has shifted to particle diameters less than 0.1 μm (Figure 5a). These PSDs are consistent with a nucleation/vaporization mechanism for Ni in the presence of chlorine. The Cr results, by contrast, show no effect on the stack PSD by chlorine, as illustrated by comparison of open and solid symbols on Figures 5b and 5c. In the case of $\text{Cr}(\text{NO}_3)_3(\text{III})$, the chlorine did not facilitate vaporization, while in the case of $\text{CrO}_3(\text{VI})$, which vaporized without chlorine, no difference in PSD was noted. The Ni and Cr results are qualitatively consistent with the equilibrium predictions of Figure 4, which show the effect of chlorine to be that of moving the Ni dewpoint from above that of Cr to below that of Cr. According to both theory and experiment, chlorine facilitates Ni volatilization at high temperatures, but has little effect on Cr. Note, however, that results are inconsistent with the low temperature equilibrium predictions of Cr with chlorine, since the Cr was found to condense at low temperature [i.e., the predicted equilibrium yield of almost 100% gaseous $\text{CrOCl}_4(\text{VI})$ and $\text{CrCl}_6(\text{VI})$ was not observed].

Scanning Electron Micrographs

In the absence of chlorine, neither $\text{Ni}(\text{NO}_3)_2$ nor $\text{Cr}(\text{NO}_3)_3(\text{III})$ appeared to vaporize, although $\text{CrO}_3(\text{VI})$ did. Yet, even in the absence of vaporization, a significant quantity of submicron particles were formed (Figure 5). The issue now is to explain how small particles are created from refractory compounds, without having recourse to vaporization/nucleation processes. Mulholland and Sarofim (1991) and Mulholland *et al.* (1991) have shown that $\text{Ni}(\text{NO}_3)_2$ can form cenospheres, which can fragment to form small particles. In their studies, this yielded a tri-modal PSD (using a cascade impactor). This tri-modal behavior was not observed here with either the impactor or the SMPS. Differences in heating rates in the two experiments are thought to account for this (Linak *et al.*, 1994).

SEM images of an exhaust particulate sample from the $\text{Cr}(\text{NO}_3)_3(\text{III})$ experiments with chlorine present (data not shown, see Linak *et al.*, 1997) show a coagulated agglomerate containing a variety of particle shapes. These images distinctly show the presence of tiny, well formed crystals, with angular sides. EDX analyses show that these elongated crystals contain Cr but no chlorine, while the fused spherical particles contain both Cr and chlorine. The mechanism by which the tiny crystals were formed, and by which chlorine is found within only a limited number of spherical particles is not known. SEM micrographs of the samples from the $\text{CrO}_3(\text{VI})$ experiments show a very finely divided amorphous powder, and were very different from those observed for the $\text{Cr}(\text{NO}_3)_3(\text{III})$ experiments. These results support the hypothesis that the two Cr species followed very different mechanistic paths from inlet to sample. However, based on sample color and low solubility, the predominant Cr species sampled for all the Cr experiments is believed to be $\text{Cr}_2\text{O}_3(\text{III})$. This was independent of whether $\text{Cr}(\text{NO}_3)_3(\text{III})$ or $\text{CrO}_3(\text{VI})$ was fed.

Sorbent Scavenging of Refractory Metals

One would not expect metals that are not vaporized to be scavenged by sorbents, such as kaolinite or lime. However, since vaporization of both $\text{Ni}(\text{NO}_3)_2$ (with chlorine) and $\text{CrO}_3(\text{VI})$ (with and without chlorine) was noted to have occurred, it is appropriate to investigate metal/sorbent interactions.

The results for Ni are especially interesting. Ni without chlorine does not vaporize (Figure 5a) and, therefore, cannot react as a vapor with kaolinite sorbent (data not shown). This is consistent with coagulation theory (Figure 2) which indicates that coagulation between small and large particles is too slow to allow metal particle scavenging by sorbent particles. When chlorine is added, Ni appears to vaporize (Figure 5a) and, consequently, it also appears to interact with kaolinite, as shown by the decrease in the very small particle mode which was present without the sorbent (Figure 5a). Hence, chlorine allows Ni to volatilize and consequently be scavenged by kaolinite. The pertinent mechanism may, however, be quite complicated, since other research (Scott *et al.*, 1992; Linak *et al.*, 1995) has shown that chlorine tends to diminish the scavenging reaction rate for Cd and Pb. These two conflicting effects must be accounted for. Figure 5a also presents the PSD for kaolinite without any other added constituent for comparison.

Similar experiments show no effect of kaolinite injection on the Cr PSD for both $\text{Cr}(\text{NO}_3)_3(\text{III})$ and $\text{CrO}_3(\text{VI})$ (data not shown). For $\text{Cr}(\text{NO}_3)_3(\text{III})$, this is not surprising, since that compound did not vaporize. However, there was also no sorbent scavenging effect on $\text{CrO}_3(\text{VI})$, even though that compound was believed to vaporize. Possible explanations include low interaction affinity between Cr and kaolinite and the possibility that the Cr vapor may not have been present long enough to contact the sorbent, which was injected downstream of the flame (see Figure 3). Figure 5 shows that Cr from $\text{CrO}_3(\text{VI})$ underwent coagulation over a longer period of time than did Ni with chlorine, presumably because it had a higher effective

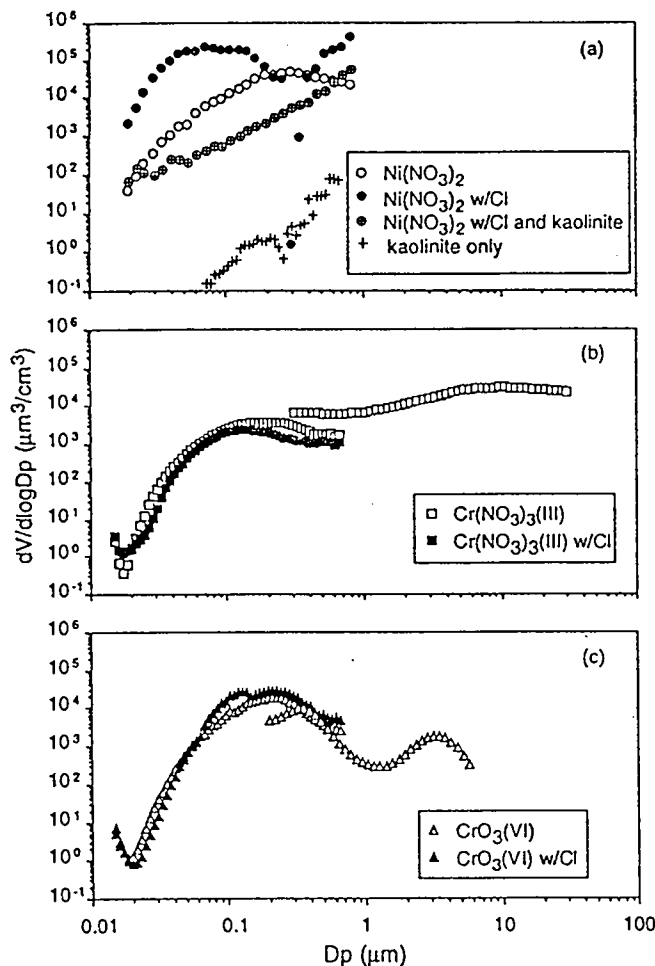


FIGURE 5 Particle volume distributions measured by electrical mobility and light scattering for: (a) $\text{Ni}(\text{NO}_3)_2$; (b) $\text{Cr}(\text{NO}_3)_3(\text{III})$; and (c) $\text{CrO}_3(\text{VI})$ aqueous solution feeds with and without kaolinite and chlorine.

dewpoint. Hydrated lime also had negligible effect on the PSDs from $\text{Cr}(\text{NO}_3)_3(\text{III})$ and $\text{CrO}_3(\text{VI})$, and so it can be concluded that lime is an ineffective sorbent for all forms of Cr tested, whether vaporization occurred or not.

Cr Speciation

In addition to factors influencing PSDs, chemical speciation is also of paramount importance, especially as far as Cr is concerned. Equilibrium predictions of Cr speciation (see Linak *et al.*, 1996) suggest that, in the absence of chlorine, the fraction of Cr(VI) is small and appears only at the higher temperatures. When chlorine is added, two additional Cr(VI) species are predicted to appear at lower temperatures ($\text{CrOCl}_4(\text{VI})$ and $\text{CrCl}_6(\text{VI})$). EDX analysis of collected particles shows that chlorine is found only on the fused spherical particles, and not on the angular crystalline particles. One might speculate that the fused particle may contain Cr compounds including $\text{CrOCl}_4(\text{VI})$ and/or $\text{CrCl}_6(\text{VI})$. However, since the equilibrium calculations at low temperatures do not predict the existence of a solid species containing Cr, one might conclude that kinetic limitations prevent significant Cr(VI) formation. Whatever the formation route to chlorinated Cr in the exhaust, sulfur is predicted by equilibrium (Figure 4) to eliminate those species and, thus, (potentially) eliminate one source of Cr(VI).

Figure 6 depicts the overall partitioning between Cr(VI) and total Cr (Linak *et al.*, 1996). In the upper panel (Figure 6a), Cr partitioning resulting from the introduction of $\text{Cr}(\text{NO}_3)_3(\text{III})$ is presented. With neither chlorine nor sulfur present, approximately 2% of the total Cr in the stack gas effluent is hexavalent. Addition of 1000 ppm (low) chlorine (stack) increased the percent Cr(VI) in the exhaust slightly to 2.5%. Addition of 6,700 ppm (high) chlorine (stack) raised the Cr(VI) percentage in the exhaust to approximately 8%. The addition of sulfur (no chlorine present) sharply diminished the emission of Cr(VI). In fact, with a high concentration of sulfur (7,900 ppm, stack), the Cr(VI) percentage was reduced to near detection levels.

The trends exhibited in Figure 6a, are consistent with equilibrium predictions, although the absolute values are not. In the absence of both chlorine and sulfur, some Cr(VI) which is stable at higher temperatures appears to persist through to the lower temperature regime, even though equilibrium would not predict its presence there. High chlorine concentrations sharply enhanced Cr(VI) emissions, possibly due to CrCl_6 which was predicted to be stable at low temperatures. The effect of sulfur is consistent with equilibrium if it is assumed that conversion of Cr to $\text{Cr}_2(\text{SO}_4)_3$ is rapid. It is interesting that equilibrium predicts that even relatively small quantities of sulfur can counteract the Cr(VI) formation tendencies of chlorine. This has been verified experimentally, where even stoichiometric quantities of sulfur were able to prevent the formation of measurable quantities of Cr(VI) (Linak *et al.*, 1997). Both theory and experiment suggest that sulfur is effective in eliminating Cr(VI) because it displaces chlorine from the Cr(VI) compounds otherwise formed without sulfur. Both theory and experiment suggest that only a very small amount of sulfur, determined by the Cr/sulfur stoichiometry, is sufficient to suppress chlorinated Cr(VI) compounds.

In the lower panel (6b), analogous results are presented for $\text{CrO}_3(\text{VI})$ feed. It is significant that they are very similar to the results presented in the top panel (6a) with Cr(III) feed. The partitioning of Cr in a combustor thus seems to be independent of the initial valence of Cr waste feed. Most of the Cr(VI) that entered was converted to Cr(III). The similarity in partitioning between the upper and lower panels of Figure 6, and the fact that the final Cr(VI)/total Cr partitioning is independent of initial speciation, suggests that prior to sampling, some type of equilibrium controlled mechanism, with neither kinetic nor mixing limitations, is operable. However, the low conversion to Cr(VI) in the presence of chlorine, and the finite conversion in the absence of chlorine and sulfur, suggest that this equilibrium is "frozen" at a temperature higher than the sampling or exhaust temperature.

SEMI-VOLATILE METALS

While non-volatile metals may not readily vaporize during combustion processes and are often reported to contribute preferentially to bottom ash and collectable portions of the PSDs, semi-volatile metals are often easily vaporized at combustion temperatures. These vapor-phase species will become supersaturated and subsequently undergo homogeneous nucleation or heterogeneous condensation at the lower temperatures downstream to contribute to the submicron PSD. These particles, because of their small size, are difficult to collect in pollution control systems. However, their propensity to vaporize also allows the possibility of control through interactions with injected sorbents. Therefore, this research investigated sorbent injection processes in which the high temperatures of practical combustion environments might be exploited to transform semi-volatile metals into constituents that are both, more easily collected, and more environmentally benign, than metal effluents in the absence of combustion modifications. Semi-volatile metals of interest were Cd and Pb, and kaolinite, bauxite, and hydrated lime were chosen as representative sorbents.

Using a downflow laboratory combustor, Scotto *et al.* (1992) found that Pb could be reactively scavenged, *in-situ*, by kaolinite powder which was injected into the post flame. Reactive scavenging (chemisorption) of a metal occurs at temperatures above the metal vapor dewpoint. This group also

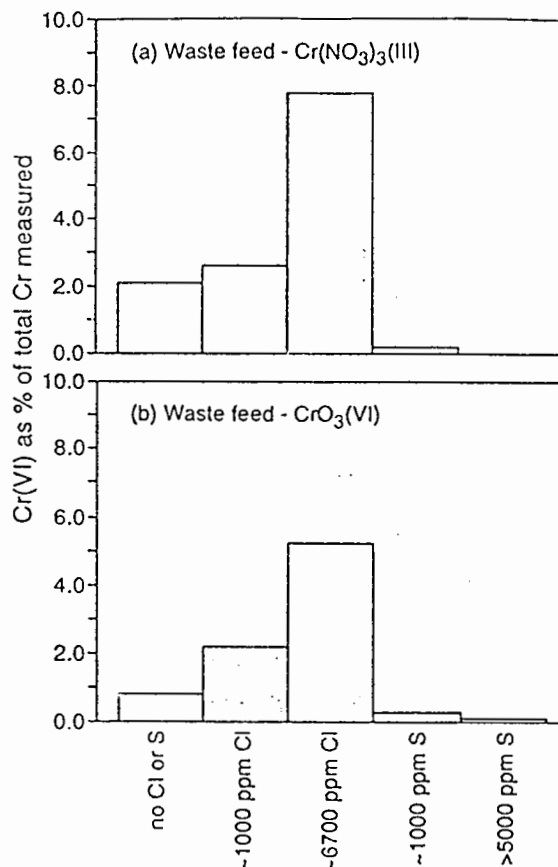


FIGURE 6 Cr(VI) mass as a percent of total Cr mass measured in the stack gases as a function of Cr waste feed valence and acid gas added: (a) $\text{Cr}(\text{NO}_3)_3(\text{III})$ waste feed; (b) $\text{CrO}_3(\text{VI})$ waste feed.

found that, although 99% of the Pb could be captured by kaolinite, the process was inhibited by the presence of chlorine. The potential use of kaolinite, bauxite, and limestone as sorbents to capture Cd and Pb was also investigated by Uberoi and Shadman (1990, 1991). Their sub-combustion temperature, fixed bed experiments suggested that kaolinite might be somewhat less effective than bauxite in capturing Cd because of pore closure caused by reaction products present in the Cd/kaolinite system but not present in the Cd/bauxite system. For the Pb/kaolinite system, the formation of a melt on the kaolinite surface appeared to enhance Pb capture. This behavior was also noted in the disperse-phase combustor experiments of Scotto *et al.* (1992). Uberoi and Shadman also found that limestone was not an effective sorbent for either Cd or Pb, although research by Ho *et al.* (1992) suggests otherwise.

Equilibrium Predictions

Figure 7 presents equilibrium predictions of the behavior of Cd and Pb in combustion environments. These calculations were made in the same manner as those for Cr and Ni presented in Figure 4. Fourteen Cd species and physical states and 20 Pb species and physical states are considered in these calculations. However, PbCl_4 was excluded for reasons explained below. In comparison to Figure 4a, equilibrium predictions (Figure 7a) indicate dewpoints of 1300 and 1200 K for 100 ppm Cd and Pb, respectively. Sulfur has a small effect on Pb, increasing its dewpoint by 100 K (Figure 7b). However, even though solid phase Cd-sulfates are stable at temperatures less than 1000 K, Cd condensation is controlled by the formation of solid phase Cd-oxide at 1300 K. Chlorine addition (Figure 7c) lowers the Pb dewpoint by 400 K and moves the Pb curve far to the left of the Cd curve. As with sulfur, chlorine affects the Cd dewpoint minimally. Even though liquid and solid phase Cd-chlorides are predicted at temperatures below 900 K, the formation of solid phase Cd-oxides dominate at higher temperatures (1300 K). Equilibrium calculations indicate that even relatively small amounts of chlorine keep Pb in the vapor form (as PbCl_2) until much cooler regions of the combustor are reached. In fact, if the species PbCl_4 were also considered as a possible species in the equilibrium calculation, then predictions would allow all of the Pb to remain as a vapor at temperatures as low as 200 K. However, Eddings and Lighty (1992) noted the absence of PbCl_4 in their experimental samples examining incineration of contaminated soils. Figure 7d indicates that, when both chlorine and sulfur are included, the Cd dewpoint remains unchanged, while the Pb dewpoint increases to 1100 K. In this system, $\text{PbSO}_4(\text{s})$ is predicted to form preferentially to $\text{PbCl}_2(\text{s})$ with a corresponding higher

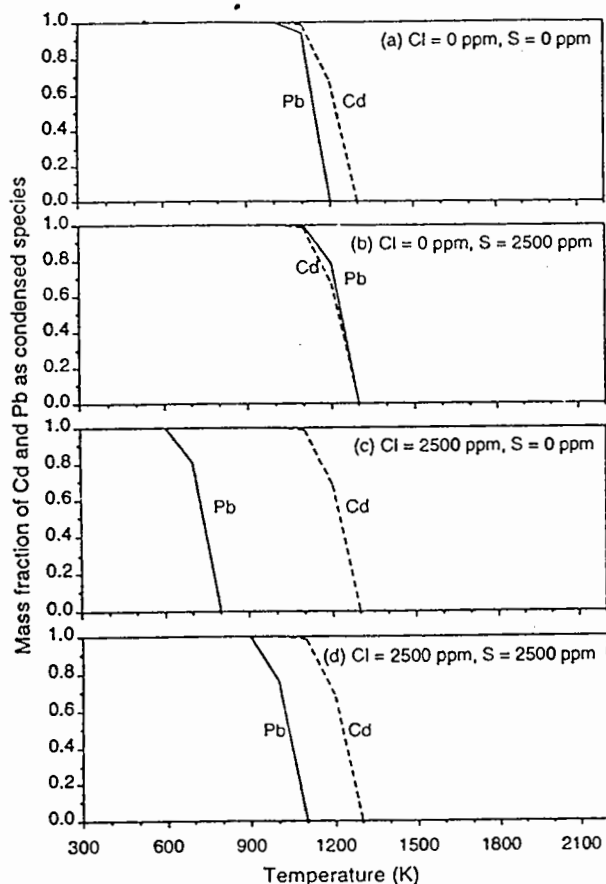


FIGURE 7 Cd and Pb equilibrium predictions for four conditions: (a) 0 ppm chlorine, 0 ppm sulfur; (b) 0 ppm chlorine, 2500 ppm sulfur; (c) 2500 ppm chlorine, 0 ppm sulfur; and (d) 2500 ppm chlorine, 2500 ppm sulfur.

dewpoint. For Cd, CdO(s) is formed at 1300 K and $\text{CdSO}_4\text{(s)}$ is preferred over $\text{CdCl}_2\text{(s)}$ forming at 1000 K.

Pb/Kaolinite/Chlorine System

In contrast to Ni (Figure 5a), the Pb data (Figure 8a), without chlorine, indicate the presence of a distinct submicron mode with a mean particle diameter between 0.1 and 0.2 μm . This behavior is consistent with Pb vaporization followed by subsequent aerosol formation and growth and is consistent with the known volatilities of elemental Pb and Pb-oxide. With chlorine added, this mode is shifted towards even smaller particle sizes (between 0.03 and 0.1 μm) possibly indicating delayed nucleation and a less mature aerosol at the sampling location. There is also evidence of bimodal behavior in the presence of chlorine which may indicate the formation of at least two Pb species with different nucleation characteristics. The impactor data (Figure 8b) indicate that between 80 and 82% of the measured Pb is associated with particles smaller than 1.1 μm .

With the addition of kaolinite, both the DMPS and impactor data indicate substantial reductions in the submicron aerosol volume and Pb mass fraction (72 and 98%, respectively) compared to the corresponding PSDs without chlorine. Similar reductions are also evident comparing the distributions with chlorine (49 and 86%). Morphological observations indicated that much of the kaolinite melted, both with and without Pb present. These results are consistent with those of Scotto *et al.* (1992), where high uptakes of Pb on sorbent particles were associated with formation of melts on sorbent surfaces.

Cd Interactions with Sorbents

Cd baseline and Cd/chlorine data (without kaolinite) are similar to corresponding Pb data presented above. Elemental Cd, CdO, and CdCl_2 vapor pressures are similar to those for elemental Pb, PbO, and PbCl_2 , all of which are notably high at the peak temperatures seen in the combustor. As with the Pb system, the Cd behavior is indicative of particle formation via a vaporization mechanism. The impactor data (Figure 9a) show that 88 and 85% of the Cd mass are associated with particles less than 1.1 μm for the Cd baseline and Cd/chlorine experiments, respectively. Also consistent with the Pb data, the Cd data show that the addition of kaolinite causes substantial decreases in both the DMPS submicron volume concentration (61%-data not shown) and the <1.1 μm impactor Cd mass fraction (97%-Figure 9a).

These results differ from those of Uberoi and Shadman (1991) in two important respects: (1) the amount of Cd removed here (97%), in a time-scale of seconds, is far higher than the 5% removed by kaolinite in their moderate temperature bench-scale studies, and (2), the sorbent particles that removed Cd here were melted, with no observable (by XRD) Cd-related crystalline structure, while in the bench-scale studies they remained crystalline. The melt appeared to avoid limitations of pore blockage by reaction products, as identified by Uberoi and Shadman (1991).

With the addition of bauxite, the DMPS distributions (Cd baseline and Cd/bauxite) illustrate significant removal of particles <0.2 μm (distributions not shown). The impactor data (Figure 9b) indicate that 97% of the Cd originally associated with particles <1.1 μm in diameter was removed from that particle size range through the addition of bauxite. These results are in agreement with those of Uberoi and Shadman (1991) which suggest bauxite to be an exceptional sorbent for use with Cd. Furthermore, in both this combustor study and in the previous bench-scale studies, the sorbent particles remained unmelted and crystalline. Therefore, sorbents that do not melt can also be effective in reactively scavenging vapor-phase metals, if pore blockage is not a factor.

As with the two other sorbents, hydrated lime acts as an effective agent to scavenge Cd which would otherwise contribute to the submicron aerosol fraction (Figure 9c). However, these results are in contrast to those of Uberoi and Shadman (1991), and one would not expect reactive scavenging to occur. It is interesting to note that hydrated lime seems to be particularly effective even in the presence of chlorine. The 99% reductions in both submicron volume (DMPS data not shown) and Cd submicron mass fraction (impactor) with chlorine present (Figure 9c), represent the greatest measured removals seen for any chlorinated system examined here. In the absence of Cd, the lime sorbent particles were crystalline, angular, and had not melted. With the addition of Cd, the calcium-rich sorbent particles melted. Calcium oxide, which is basic, is known to enhance formation of eutectic melts with acidic metal oxides.

Mechanisms and Conclusions

There appear to be two high temperature mechanisms that allow the scavenging of metals at combustion temperatures above their dewpoints. The first mechanism involves reaction between metal vapor and a sorbent

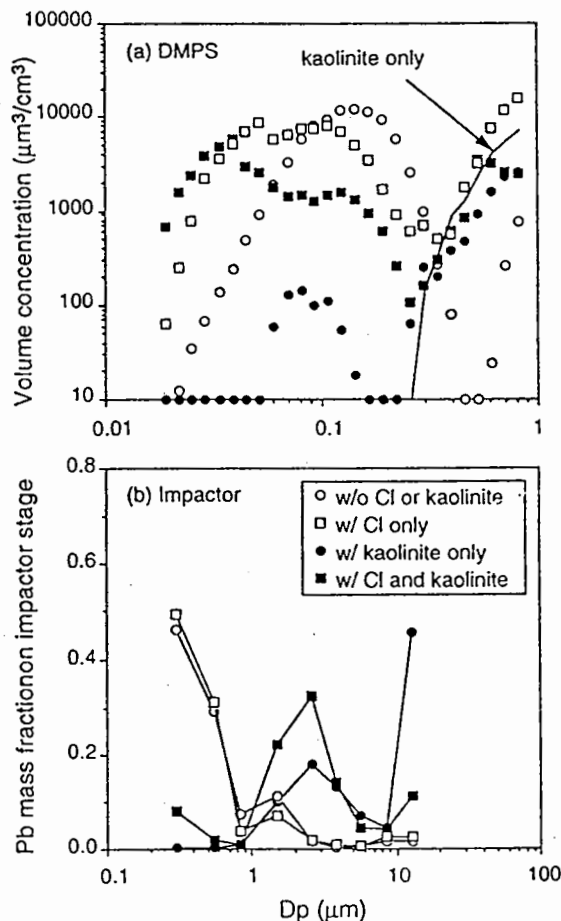


FIGURE 8 DMPS submicron volume distribution and impactor Pb mass fraction distribution for the Pb/kaolinite/chlorine system.

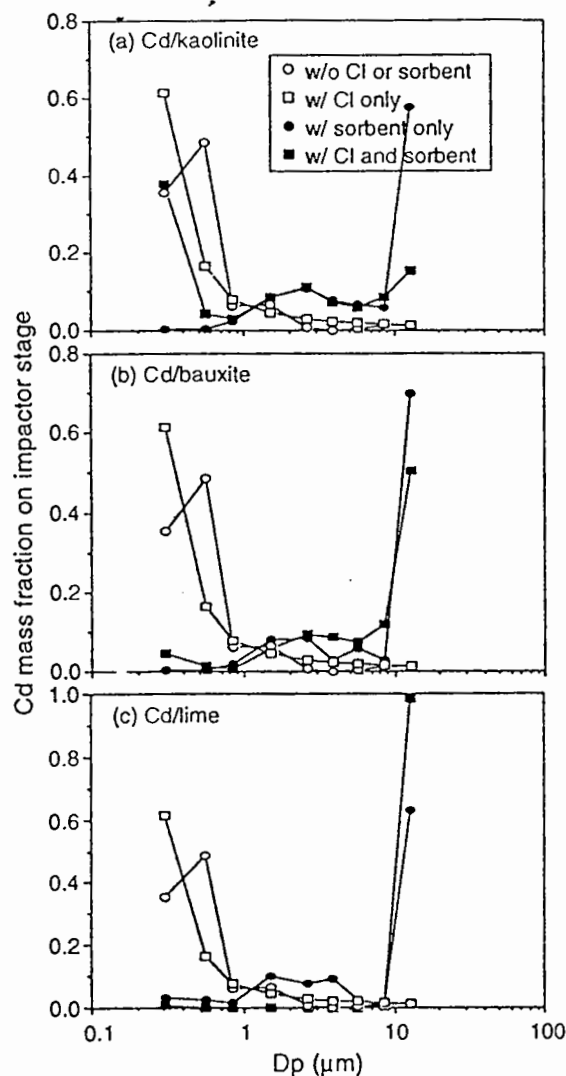


FIGURE 9 Interactions between Cd and three sorbents. Impactor mass fraction distributions for: (a) Cd/kaolinite; (b) Cd/bauxite; and (c) Cd/lime, with and without chlorine.

crystalline surface (Uberoi and Shadman, 1991). SEMs provided evidence of this sorption mechanism for the Cd/bauxite system, which, by exhibiting a $1/D_p$ dependence of Cd mass fraction on the sorbent, also suggested pore diffusion or external reaction controlled processes (Linak and Wendt, 1993). The second mechanism allows scavenging of metal vapor by a liquid melt on the sorbent. Melting appears to improve capture. Cd was scavenged by kaolinite in the combustor used here, because the sorbent melted (as depicted in SEMs), but it was only poorly scavenged at lower temperatures (Uberoi and Shadman, 1991) where no melting was observed. In the Cd/lime system, the melt was created by the very interaction of dissolution. Melts were also observed after the scavenging of labile Ni (in the presence of chlorine). Thus, metal capture by sorbents may be more practical in high temperature combustion environments, where melting is more likely, than was initially suggested by the moderate temperature bench-scale thermogravimetric reactor studies (Uberoi and Shadman, 1990, 1991).

The effect of chlorine is to significantly increase the submicron volume concentrations and submicron metal mass fractions, in the absence of sorbents, and, for the Pb/kaolinite, Cd/bauxite, and Cd/kaolinite systems, to diminish sorbent effectiveness when they are present. An explanation for this behavior is as follows: for Pb and Cd interaction with aluminosilicate sorbents, the true metal reactant with the substrate is probably the metal hydroxide or oxide. As chlorine is introduced, equilibrium is shifted away from these reactive metal species towards unreactive metal chlorides. This has been shown for the Na/kaolinite system (Mwabe, 1993), and suggested for Pb (Scotto *et al.*, 1992). Ni, however, can be vaporized only by interaction with chlorine, and then (possibly through equilibrium with other reactive Ni species) scavenged by kaolinite. The capture of Cd by hydrated lime is through a different (physical) mechanism (suggested by the SEMs) where the pertinent mechanisms involving chlorine are currently unknown.

VOLATILE METALS

Volatile metals including Hg and Se can be distinguished from semi-volatile metals in combustion systems by the fact that they exhibit significant vapor pressures even at low to moderate temperatures typical of flue gas cleaning equipment. This typically results in poor emission control of these species. In fact, of all the trace metals emitted during fossil fuel combustion and waste incineration processes, Hg is likely considered the most problematic. This is not because it is the most toxic or typically present in highest concentrations, but rather, because current control processes designed for particulate, nitrogen oxide (NO_x), and acid gas emissions are minimally effective in controlling vapor-phase Hg species.

Hg exists in two valent states: elemental Hg (Hg^0), and oxidized (ionic) Hg (Hg^{+2}). Effective Hg control using methods designed for particulate and acid gas emissions will depend largely on the form (vapor or condensed phase) and speciation (elemental or oxidized) of the Hg in post-combustion regions prior to air pollution control devices. It has been noted by Senior *et al.* (1997) that oxidized Hg^{+2} is more likely to be captured by residual carbon or removed by existing flue gas desulfurization units, while elemental Hg^0 is more likely to escape the air pollution control devices and be emitted to the atmosphere. Several investigations are in progress examining the potential of carbon and inorganic-based sorbents for Hg control at moderate to low temperatures typical of flue gas cleaning systems (Miller *et al.*, 1995; Krishnan *et al.*, 1995, 1997).

Equilibrium Predictions

Figure 10 presents equilibrium predictions of the behavior of Hg within a combustion environment. Sixteen Hg species and physical states were considered. These calculations were made in the same manner as those presented for the non-volatile and semi-volatile metals (Figures 4 and 7), with the exception that the Hg concentration (stack) used was 100 ppb instead of 100 ppm. Methane/air combustion at a stoichiometric ratio of 1.2 was used. Chlorine and sulfur concentrations (stack) were both 100 ppm. The top two panels (Figures 10a and 10b) plot condensed mass fraction of Hg and oxidized Hg^{+2} mass fraction as a function of temperature. Four conditions (with and without chlorine and sulfur) are presented on each panel. Figure 10a indicates a Hg dewpoint (without chlorine or sulfur) between 400 and 500 K through the condensation of $\text{HgO}(s)$. The effect of sulfur is to increase this threshold temperature approximately 100 K, while the effect of chlorine (even with sulfur present) is to decrease the Hg dewpoint through the formation of $\text{HgCl}_2(s)$. Note that, in contrast to Cr, $\text{HgSO}_4(s)$ is not preferred to $\text{HgCl}_2(s)$. Figure 10b indicates that at high temperatures (>900 K) almost all the Hg exists as Hg^0 . Without chlorine or sulfur, HgO and then $\text{HgO}(s)$ are predicted with decreasing temperature. With sulfur (but without chlorine), HgO and then $\text{HgSO}_4(s)$ are predicted. However, HgO , HgCl_2 , and then $\text{HgCl}_2(s)$ are predicted to be formed whenever chlorine is available (<900 K), and vapor-phase HgCl_2 is predicted to be present as the dominant Hg species at temperatures between 900 and 400 K. This may offer the possibility of Hg control through interactions of oxidized HgCl_2 with sorbents.

It should be re-emphasized that equilibrium calculations can be used only to determine which species are thermodynamically possible. They do not include kinetic or mixing considerations which may severely limit the attainment of equilibrium in the short times available in practical combustion systems. Senior *et al.* (1997) report that, in a survey of 14 coal combustion systems, oxidized Hg^{+2} concentrations upstream of the air pollution control devices (750-900 K) ranged between 30 and 95% of the total Hg measured (averaging 75%). They went on to conclude that equilibrium could not be used to quantitatively predict Hg speciation in the flue gas. However, even with this liability, equilibrium calculations are useful to test hypotheses and suggest experiments.

Figures 10c and 10d present the results of equilibrium calculations designed to examine possible interactions between Hg and calcium that might be present in the ash or introduced as a sorbent. While searching thermodynamic data bases for data on Hg species, we discovered data for a set of calcium-Hg amalgams (TAPP, 1995), and these "species" were included in the data base for the calculations presented in Figures 10c and 10d. Figure 10c presents predicted Hg speciation as a function of temperature for a fuel-lean ($\text{SR}=1.2$) scenario with calcium. Sulfur was also included because of its possible interactions with calcium. As expected calcium oxides, hydroxides, carbonates, and $\text{CaSO}_4(s)$ are the preferred species over all temperatures examined. However, under fuel-rich conditions, such as those used to stage combustion for NO_x control, these oxidized species are not predicted, and Figure 10d indicates that two calcium-Hg amalgams are thermodynamically stable within a temperature window between 900 and 1300 K. This result may be significant because it represents conditions that may be achieved in practical combustion systems. Experiments are currently underway to examine these predictions. Other experiments are examining Hg speciation as functions of combustion conditions and chlorine and sulfur content, and factors which promote the formation of Cl_2 over HCl which may influence concentrations of HgCl_2 (Gullett *et al.*, 1990; Senior *et al.*, 1997).

Preliminary experiments (without chlorine or sulfur addition) indicate that Hg speciates primarily as elemental Hg^0 (>95%) and that hydrated lime (introduced as a sorbent) is minimally effective in reducing the vapor-phase oxidized Hg^{+2} under fuel-lean ($\text{SR}=1.2$) conditions. However, similar

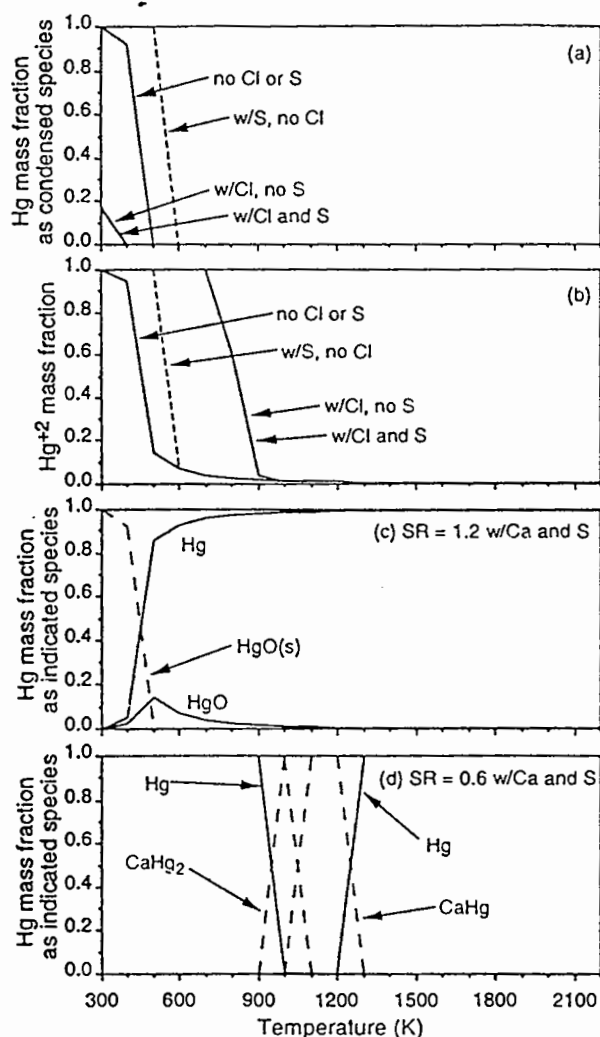


FIGURE 10 Hg equilibrium predictions: (a) condensed fraction with and without chlorine and sulfur; (b) oxidized fraction with and without chlorine and sulfur; (c) Hg species with calcium and sulfur - fuel lean (SR=1.2); and (d) Hg species with calcium and sulfur - fuel rich (SR=0.6).

experiments performed under staged conditions ($SR_{primary}=0.8$) suggest that hydrated lime might be an effective sorbent, indicating that vapor-phase oxidized Hg^{+2} was reduced to less than detection limits. However, these same experiments also indicated that the elemental Hg^0 remained >95% of the total Hg measured and was unaffected by the presence of hydrated lime. Therefore, the focus of ongoing efforts includes strategies to promote the formation of oxidized Hg^{+2} species (through, for example, chlorine and sulfur addition) in an effort to improve the effectiveness of calcium based sorbents.

ACKNOWLEDGMENTS/DISCLAIMER

I would like to gratefully acknowledge the contributions of Jost O.L. Wendt of the University of Arizona who has collaborated in these research efforts since their onset. The research described in this article has been reviewed by the Air Pollution Prevention and Control Division, U.S. Environmental Protection Agency, and approved for publication. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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NRMRL-RTP-P-250		TECHNICAL REPORT DATA (Please read Instructions on the reverse before comp)	
1. REPORT NO. EPA/600/A-97/085		2.	
4. TITLE AND SUBTITLE Metal Partitioning in Combustion Processes		5. REPORT DATE	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) William P. Linak		8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS See Block 12		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO. NA (Inhouse)	
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air Pollution Prevention and Control Division Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Published paper; 10/89-6/97	
		14. SPONSORING AGENCY CODE EPA/600/13	
15. SUPPLEMENTARY NOTES APPCD project officer is William P. Linak, Mail Drop 65, 919/541-5792. Presented at 4th Int. Conf. on Technologies and Combustion for a Clean Environment. Lisbon, Portugal, 7/7-10/97.			
16. ABSTRACT The paper summarizes ongoing research efforts at the National Risk Management Research Laboratory of the U.S. Environmental Protection Agency examining (high temperature) metal behavior within combustion environments. The partitioning of non-volatile (Cr and Ni), semi-volatile (Cd and Pb), and volatile (Hg) metals in combustion systems was investigated theoretically and experimentally. Theoretical predictions were based on chemical equilibrium and suggested that such calculations can be useful in predicting relative volatility and speciation trends, and to direct experimental efforts. Equilibrium studies employing a 59 kW laboratory scale combustor examined the behavior (volatility, particle size, and speciation) of metal vapors and particles produced by aqueous metal solutions sprayed through a swirling natural gas diffusion flame. These experiments were designed to study metal transformation mechanisms in a relatively simple combustion environment without the complex effects of additional species. Further experiments examined the potential use of common inorganic sorbents (kaolinite, bauxite, and hydrated lime) to adsorb metal vapor, offering a potential means of metal emissions control.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Metals Emission Separation Combustion Volatility		Pollution Control Stationary Sources Trace Metals Partitioning	13B 11G 11F, 07B 14G 21B 20M
18. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES
		20. SECURITY CLASS (This page) Unclassified	22. PRICE