PREDICTION OF THE FATE OF TOXIC METALS IN WASTE INCINERATORS

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ABSTRACT

The EPA and state governmental agencies are investigating means of controlling the emissions of toxic metals from waste incinerators. In order to aid in the development of effective regulations and control strategies, an analytical procedure to estimate the emission of metals from combustion devices is being developed. The procedure includes analysis of key phenomena such as particle entrainment, metal vaporization, vapor condensation, particle coagulation and particle removal by flue gas cleaning equipment. This paper describes the components of the procedure, discusses its application to identify key parameters, and compares model predictions with experimental data.

INTRODUCTION

The emission of toxic metals during the incineration of metal bearing wastes presents a potential health hazard of increasing interest to federal and state regulatory agencies. The emitted metals are often concentrated on the particles with diameters of less than 1 μm [1]. This significantly enhances the threat posed by the metals, since air pollution control equipment is less efficient at capturing these small particles and particles of this size are most likely to be deposited in the lungs [2].

The U.S. Environmental Protection Agency (EPA) has published proposed regulations for restricting the burning of metal bearing wastes in boilers and industrial furnaces based on dispersion modeling and worst case risk assessment [3]. Similar regulations or guidelines are likely to be forthcoming for hazardous and municipal waste incinerators. State and local agencies often follow the EPA's lead and institute their own regulations restricting the emissions of toxic metals. This body of regulations is likely to affect the majority of the incinerators in the U.S., since nearly every waste contains at least trace quantities of some toxic metals.

A procedure for predicting the behavior of toxic metals during the incineration of metal-bearing wastes could aid governmental agencies in the development of appropriate regulations and could help incinerator operators develop effective strategies for minimizing emissions from their incinerators. In order to develop such a procedure, however, it is first necessary to determine the key phenomena that control the behavior of metals during the incineration of waste materials. By examining the characteristics of emissions from a wide variety of incinerators, it is possible to identify many of the mechanisms that play important roles in controlling the behavior of the metals. Figure 1 illustrates these mechanisms.

Inorganic material often contains most of the metals and metal species present in a waste. A large fraction of the inorganic material remains inert during incineration and forms ash particles [4]. If the waste is a liquid burned in a liquid injection incinerator, nearly all of the ash particles are small and are entrained by the gas flow [5]. If the waste is initially a solid, some fraction of the smaller particles are entrained while the remaining material is removed from the combustion chamber as residual ash. The quantity of material entrained is a function of the size, shape, and density of the ash particles as well as the incinerator operating conditions [6]. For liquid and solid wastes the entrained particles can range in size from 1 μm to over 50 μm. However, they are generally less than 20 μm in diameter [5, 7].

Some metals and metal species found in waste materials are relatively volatile and vaporize under the conditions encountered in the incinerator [8]. This behavior is probably independent of the physical form of the waste. The vapors are carried away from the waste by the exhaust gas and recondense as the gas cools. The vapors condense both homogeneously to form new particles and heterogeneously on the surfaces of the entrained ash particles [9]. Homogeneous condensation produces small particles less than 1 μm in diameter [10]. Heterogeneous condensation also tends to favor small particles due to their higher surface area [11]. Thus the small entrained particles have higher concentrations of volatile metals than either large particles or the original waste. The concentration of some metals in the small particles is as much as one hundred times greater than in the original waste [12].

Metals may exhibit a third type of behavior during the combustion of waste materials. A high temperature, reducing environment is created near the burning waste even though the incinerator is operated at an overall excess air condition [4]. The exact conditions in this area depend on the physical characteristics of the waste and the configuration and operation of the incinerator. Under these conditions, some metal species react to form new compounds such as metal chlorides, sulfides, and reduced species [4]. These new compounds are often more volatile than the original species and vaporize. Once the vapors move away from the waste and encounter the lower temperatures and higher oxygen concentrations found in the exhaust gases, they may undergo secondary reactions, convert back to their original form, and condense [9]. As with the volatile metal species, both homogeneous and heterogeneous condensation occurs.

A procedure based on the mechanisms illustrated in Fig. 1 has been developed to estimate the emissions of metals from the incineration of metal-bearing wastes. This paper describes the analytical approach and discusses the application of the procedure to: *(a)* identify the variables which most strongly influence metals emissions; and *(b)* compare predictions with experimental measurements to ascertain the accuracy of the approach.

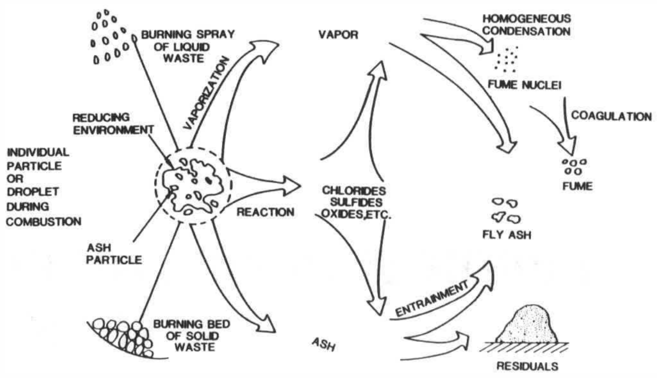

FIG. 1 TRANSFORMATION OF MINERAL MATTER DURING COMBUSTION OF METAL CONTAINING WASTE

ANALYTICAL APPROACH

The procedure consists of a group of computer models and analytical approaches. These models simulate the physical and chemical processes which occur in the incineration of metal-bearing wastes. The phenomena simulated include:

(a) Reactor thermal behavior.
(b) Particle entrainment.
(c) Metals reactions and vaporization.
(d) Aerosol dynamics.
  (1) Condensation.
  (2) Coagulation.
(e) Particle capture.

Figure 2 illustrates the relationship between these mechanisms and the operation of a typical grate-type furnace.

Initially the temperature history of the incinerator must be established in order to determine the background environment for the burning waste and the post-flame temperature history of the condensing metal vapors. A number of computer models capable of estimating the thermal behavior of an incinerator are either available or are under development. These models vary widely in complexity from relatively simple zero-dimensional approaches [13] to extensive three-dimensional models [14]. An appropriate model is selected based on the amount of information available and the degree of accuracy that is desired.

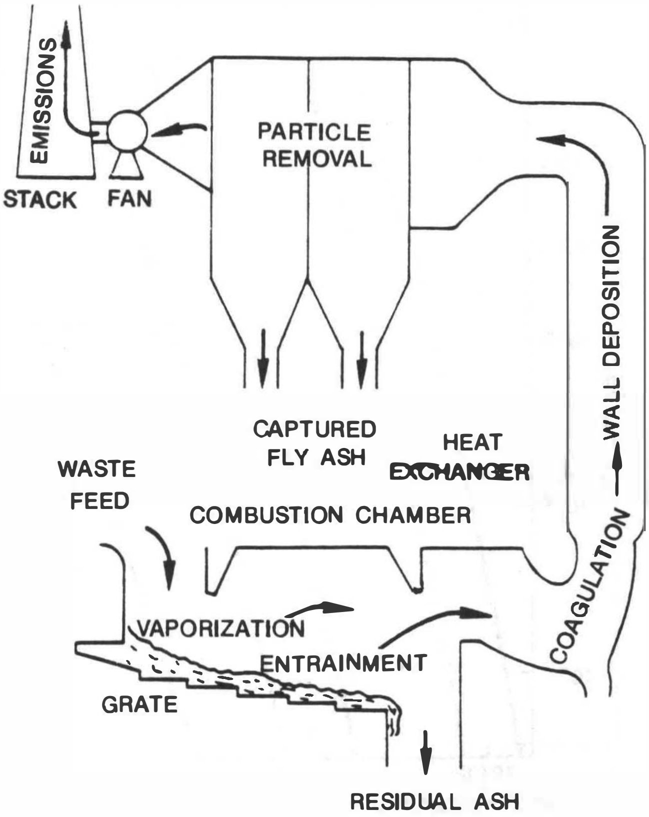

FIG. 2 KEY PHENOMENA CONTROLLING THE BEHAVIOR OF METALS IN A GRATE-TYPE INCINERATOR

The local temperature encountered in the vicinity of the burning waste is also important and must be estimated. However, the behavior of the burning waste is strongly influenced by the physical form of the waste being incinerated. In general, wastes can be classified into one of five categories based on their physical form. These categories are:

(a) Liquids.
(b) Liquid-solid mixtures.
(c) Homogeneous solids.
(d) Heterogeneous solids.
(e) Containerized materials.

Homogeneous solids consist of particles that are relatively uniform in size and composition. Heterogeneous solids vary widely in both size and composition. Some procedures exist for modeling the incineration of liquids in spray flames [15], but no effective modeling procedures are available for the other waste forms. Thus the temperatures in these wastes must be estimated based on the bulk temperature and the adiabatic flame temperature.

Once the temperatures are established, the quantities of metal species that vaporize directly or react and vaporize can be determined. The approach in this determination is based on two assumptions: *(a)* all reactions achieve equilibrium at local conditions; and *(b)* all elements contained in the waste are intimately mixed. The program developed by NASA's Lewis Research Center, CET85 [16], is used to determine the equilibrium behavior of the metals in the waste under combustion conditions.

The amount of ash entrained depends on the size, shape and density of the ash as well as the operating characteristics of the incinerator. Li [6] developed an approach that is used to estimate the entrainment from rotary kiln incinerators. Approximations are made for entrainment for other incinerator types based on particle settling velocities and gas flow rates.

Condensation is a key process since it accounts for the enrichment of metals on small particles. A computer model accounting for both homogeneous and heterogeneous condensation has been developed. The rate of homogeneous condensation is predicted using the classical Becker-During approach as presented by Friedlander [10]. The approach used to model heterogeneous condensation depends on the size of the particles onto which the material is condensing. For particles much smaller and much larger than the mean free path of the gas (0.25 μm) expressions derived by Friedlander [10] based on the kinetic theory of gases and gas phase diffusion, respectively, are used. For particles with diameters approximately the same size as the mean free path of the gas, a transition expression developed by Fuchs and Sutugin and described by McNallan et al. [17] is used.

As the particles formed by homogeneous condensation and the entrained particles move through the incinerator they collide both with one another and with the vessel's walls. Often the colliding particles stick together and form a single larger particle. Similarly, many of the particles which collide with the walls stick to them and are consequently removed from the gas flow. Particle coagulation and wall capture are simulated using a computer model developed by Gelbard [18].

Finally the removal of particles from the gas stream by the air pollution control device (APCD) associated with the incinerator must be accounted for. The efficiency of particle removal typically depends on the particle size distribution and on the design and operation of the APCD. A wide variety of APCDs are used. Each is based on a different basic mechanism. Computer models have been developed or obtained for the following APCDs:

(a) Electrostatic precipitators.
(b) Venturi scrubbers.
(c) Cyclones.
(d) Baghouses.
(e) Baffle plate scrubbers.

The models have been obtained from a variety of sources. A detailed discussion of these models is beyond the scope of this paper.

SENSITIVITY STUDIES

A sensitivity analysis was conducted to identify important parameters affecting the partitioning of metals in waste incineration. Parameters considered include:

(a) Combustor temperature.
(b) Waste chlorine content.
(c) Saturation ratio.
(d) Entrained particle size distribution.
(e) Gas residence time.
(f) Waste sulfur content.

The temperature of the burning waste has one of the strongest effects on the predicted behavior of the metals. Figure 3 illustrates the impact of temperature on some representative metals' effective vapor pressures. The effective vapor pressure determines the quantity of material that vaporizes and subsequently condenses. It depends on the most stable chemical form of the metal under the conditions considered. As temperature increases vapor pressure increases, resulting in increased metals emission. The curves in Fig. 3 were determined based on a local stoichiometric ratio of 1.0 as is expected near the burning waste. Under these conditions, metals are predominantly in the form of their oxides.

Several features of the curves in Figure 3 warrant attention. First the vapor pressures of all the metals increase sharply with temperature. A ten-fold increase in the vapor pressure can result from a temperature increase as small as 20 K. Second, the vapor pressures vary widely from metal to metal. Third, all of the vapor pressures shown are very small. This indicates that only a small quantity of each metal will vaporize. However, due to the enrichment of vaporized species on small particles, the ability of small particles to penetrate deep into the lung, and the toxicity of many of the metals, a small quantity of vaporized material is sufficient to constitute a potential health threat.

The quantity of chlorine in the waste was found to have a significant effect on the vapor pressure of many metals. Figure 4 indicates the behavior of several representative metals under typical combustor conditions. In general, chlorides are more volatile than the corresponding metal oxides or uncombined metals. Thus, the effective vapor pressure of the metal is increased as the concentration of chlorine increases and more of each metal is converted to metal chloride. However, once the metal has been totally converted into metal chloride, the presence of additional chlorine has no effect on the vapor pressure of the metal. In Fig. 4 the curves for chromium, nickel, strontium and copper reflect this type of behavior. The vapor pressures increase rapidly with chlorine concentration at low chlorine concentrations, but level off at higher concentrations.

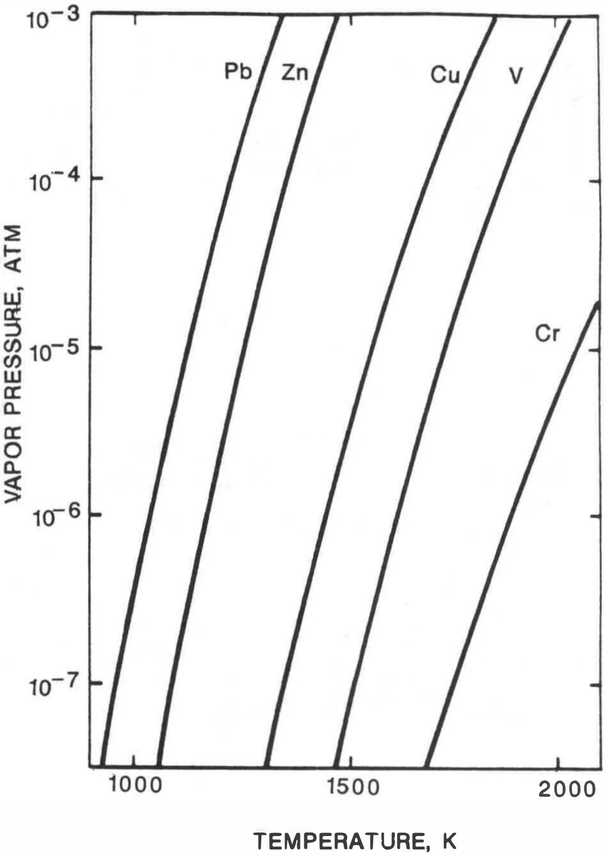

FIG. 3 EFFECT OF TEMPERATURE ON THE VOLATILITY OF REPRESENTATIVE METALS

Heterogeneous and homogeneous condensation occur simultaneously at different rates. All of the material that condenses homogeneously forms particles less than 1 μm in diameter, whereas the distribution of the material that condenses heterogeneously depends on the size distribution of the entrained particles. Some heterogeneous condensation occurs on larger particles, which are effectively captured by the APCD. Thus

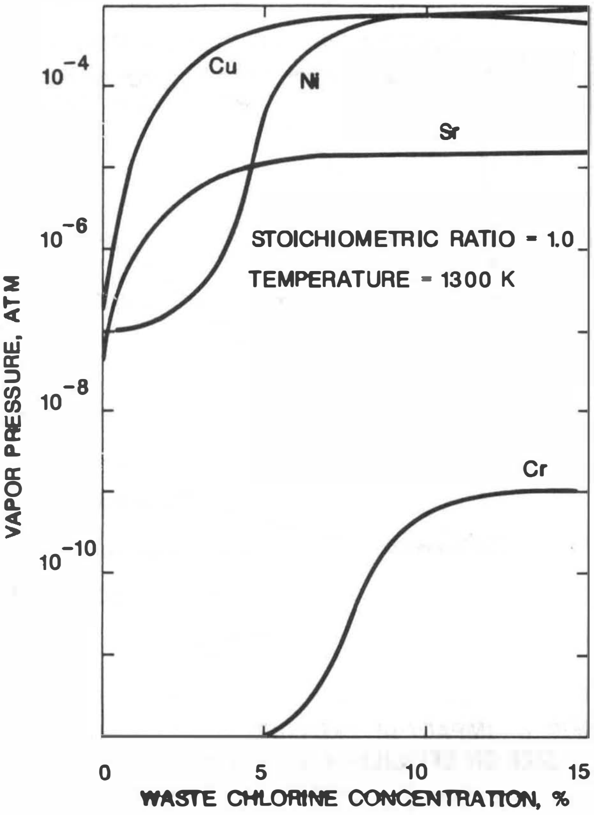

FIG. 4 IMPACT OF CHLORINE ON THE VOLATILITY OF REPRESENTATIVE METALS

metal emissions increase as the ratio of homogeneous to heterogeneous condensation increases.

Condensation ratio is defined as the ratio of the homogeneous condensation rate to the heterogeneous condensation rate. One of the most important parameters controlling the condensation ratio is the ratio of the actual concentration to the equilibrium concentration of the metal in the vapor phase, defined as the saturation ratio. Thus, in order for condensation to occur, the saturation ratio must be greater than 1.0. High saturation ratios result when there is rapid cooling or when a metal reacts suddenly to form a relatively nonvolatile species. This second mechanism occurs when a nonvolatile metal oxide reacts in the reducing atmosphere in the vicinity of the burning waste to form a volatile species which subsequently vaporizes, moves away from the waste, and then reacts again to form the original nonvolatile metal oxide.

Figure 5 shows the impact of the saturation ratio on the condensation ratio. In Fig. 5, T is the bulk temperature, P_{sat} is the saturation vapor pressure, and SA is the available particle surface area. The available particle surface area is defined as the sum of the surface areas of all particles in a given volume of gas. The value of SA, 7×10^{-14} m²/m³, corresponds to 1000 particles 5 μm in diameter per cubic meter of gas. The sensitivity study shown in Fig. 5 used typical bulk combustor conditions and a simplified entrained particle size distribution. The simplified size distribution was used to simplify the analysis since relative rather than absolute effects were of interest. At low saturation ratios the condensation rates are approximately equal. However, as the saturation ratio increases, the rate of homogeneous condensation increases rapidly. Nearly 90% of the condensation is homogeneous at a saturation ratio of about 4.0. As the saturation ratio con-

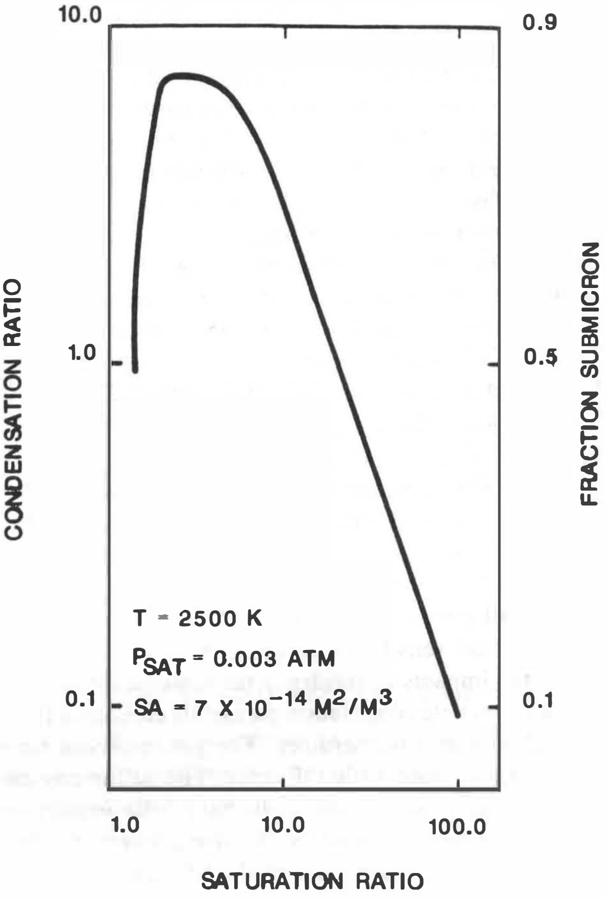

FIG. 5 IMPACT OF SATURATION RATIO ON CONDENSATION

Condensation Ratio is the Ratio of Homogeneous to Heterogeneous Condensation Rate and Submicron Fraction is the Fraction of the Condensing Material Forming Submicron Particles.

tinues to increase heterogeneous condensation again becomes more important.

The APCD's performance plays a vital role in determining the quantity of particulates emitted by an incinerator. The efficiency of each device is a function of its operating parameters and the size distribution of the entrained particles. Figure 6 shows the effect of pressure drop, a key operating parameter, and particle size on the collection efficiency of a typical venturi scrubber. The calculations were performed with a venturi scrubber model based on the semi-empirical of Calvert [19]. Values typically found in industrial venturi scrubbers were used for other parameters such as liquid-to-gas ratio and gas velocity. The collection efficiency increases with pressure drop for all sizes of particles. However, the efficiency is small for particles less than 1 μm in diameter. The particles typically formed by homogeneous condensation, those around 0.1 μm [4], are collected with efficiencies of less than 40% at all pressure drops examined.

Additional sensitivity analyses were conducted to assess the impacts of residence time, waste sulfur content and particle coagulation on metals emissions from hazardous waste incinerators. The gas residence time was found to exert little influence. The sulfur content of the waste was determined to have little impact on the vaporization of metals. Sulfur does, however, affect the dewpoint and resistivity of the effluent which may impact APCD performance. Coagulation was found to be too slow to significantly affect the size distribution of the entrained particles within the residence times typically encountered in incineration systems.

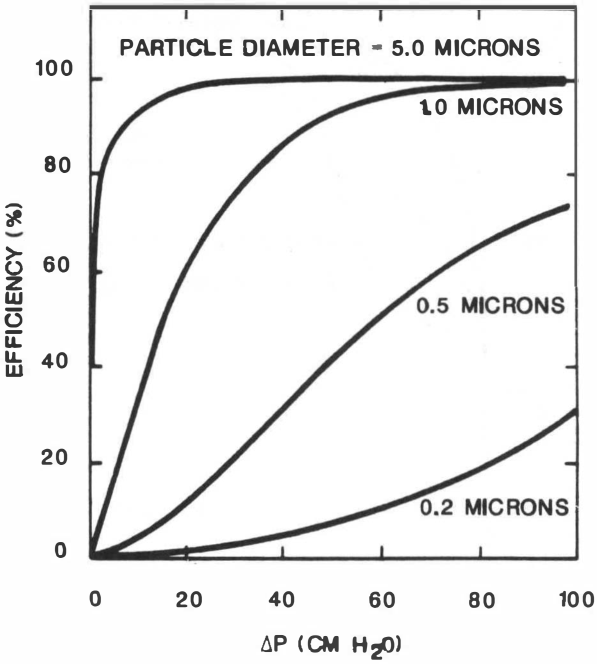

FIG. 6 IMPACT OF PRESSURE DROP AND PARTICLE SIZE ON EFFICIENCY OF A VENTURI SCRUBBER

COMPARISON WITH EXPERIMENTAL DATA

A complete data set which can be used to verify the analytical procedure is not available. However, some idea of the method's accuracy can be obtained by using data from experimental studies which did not obtain all of the input data needed by the procedure and making reasonable estimates of the remaining data. One applicable data set was compiled by Brunner and Monch [20], who analyzed the partitioning of several metals in a large municipal solid waste incinerator. The incinerator is similar to that shown in Fig. 2. It has a nominal system capacity of 192 metric tons per day. The waste used was generated by a partially rural area and was subjected to no pretreatment. The residual ash was sampled after quenching and the captured fly ash was removed directly from the electrostatic precipitator hoppers. The entrained particles were sampled isokinetically and collected on quartz wool. Concentrations of metals in the particles were determined using ion-coupled plasma spectrometry. Gaseous metals in the exhaust stream were captured by sorption in 0.1 N sodium hydroxide and were measured using atomic adsorption spectroscopy. One of the principal parameters which could not be calculated was the quantity of material entrained. Since iron was not expected to vaporize under the conditions encountered in the incinerator, the experimentally measured quantity of iron in the captured and emitted fly ash was used to estimate the amount of entrainment occurring.

Figure 7 shows how the predictions produced using suitable approximations compare with the experimental results for some typical metals. The metals in the waste are divided between three streams: residual ash, captured ash and emitted ash. The residual ash is collected at the end of the combustion chamber and consists of nonreactive and nonvolatile species. The captured ash is made up of particles removed from the gas stream by the electrostatic precipitator. It consists primarily of the larger entrained particles and a fraction of the small particles formed by condensation. The emitted particles consist of some of the small entrained particles and any of the particles formed by condensation processes that are not captured by the electrostatic precipitator.

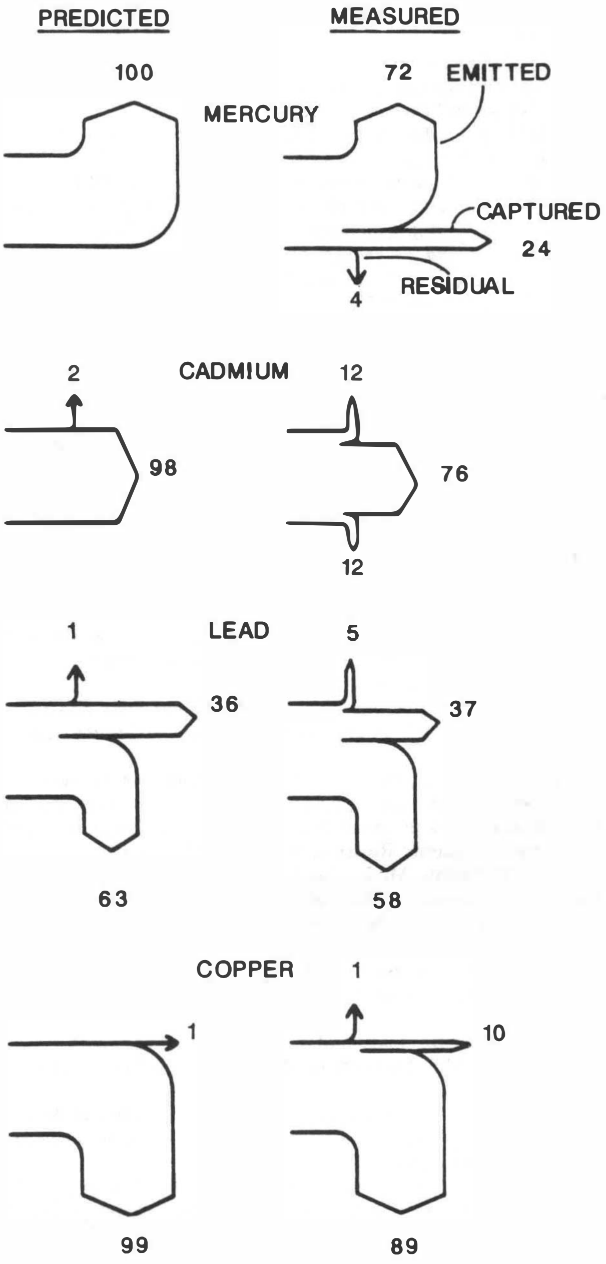

FIG. 7 COMPARISON OF PREDICTED AND MEASURED DISTRIBUTIONS OF METALS BETWEEN THE WASTE STREAMS OF A MUNICIPAL SOLID WASTE INCINERATOR

The predictions correctly identify the major mode of emission for each metal. Mercury is found primarily in the emitted particles, cadmium in the captured ash and copper in the residual ash. Lead is split between the residual ash and the captured ash. The assumptions involved in the analytical procedure itself and the approximations required for this particular analysis could potentially account for the difference between the predicted fractions of each metal in each stream and the observed values. However, the qualitative agreement obtained indicates that the analytical procedure correctly accounts for the key phenomena.

Several studies are being conducted or have been completed which examine the emission of metals from waste incinerators [12, 21, 22]. In general, these studies have found higher concentrations of several volatile metals in submicron particles than in larger particles or in the original waste. The toxic metals commonly found to be concentrated on the small particles are antimony, arsenic, cadmium, copper, lead, silver, and zinc. This is in qualitative agreement with the metals partitioning model which predicts that these metals vaporize at relatively low temperatures and recondense on the surfaces of small particles.

CONCLUSIONS AND RECOMMENDATIONS

An analytical procedure has been developed to estimate the partitioning of metals into different effluent streams during waste incineration. Sensitivity analyses indicate that high incinerator temperatures, high cooling rates, high waste chlorine concentrations, and small entrained particles all increase the quantity of metals contained in the small particles emitted into the atmosphere. Comparison of the predictions with the results of experimental studies indicates that the procedure accounts for the key phenomena but that additional refinement is needed.

The procedure has a number of potential applications both in the design and operation of incinerators which minimize the emissions of metals and in the development of effective regulations to restrict the metals emissions. Among these applications are:

(a) Prediction of emission modes from a given incinerator.

(b) Evaluation of the feasibility of new control concepts.

(c) Determination of principal permitting concerns for a given incinerator.

(d) Determination of appropriate monitoring and control parameters.

The modeling procedure is useful in its present form; however, the accuracy and utility of the predictions could be increased by improvements in the following areas:

(a) Prediction of local temperature and oxygen concentrations in the vicinity of burning wastes.

(b) Incorporation of kinetic and diffusional limitations in addition to equilibrium into the metals reaction/vaporization model.

(c) Expansion of the APCD modeling capabilities to include treatments of a wider variety of devices.

In addition to the modeling work the following experimental studies are needed to provide the data necessary to tune and verify components of the modeling procedure:

(a) Determination of the behavior of burning solid wastes.

(b) Metals reaction kinetics studies.

(c) Determination of the quantity and size distribution of particles entrained in various types of incinerators.

(d) Large scale metals emission studies.

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