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Project Summary

Inorganic Compound Identification of Fly Ash Emissions from Municipal Incinerators

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Particulate matter emitted as fly ash from municipal refuse and sludge incineration operations consists largely (>90 percent) of inorganic substances, including soot. Although it is evident from the compositions of the wastes being incinerated that chlorides, sulfates, and, in the case of sludge, phosphates are potential reactant products in the combustion process, the inorganic particulate emissions frequently are referred to as metallic oxides. Actual inorganic speciation of complex environmental samples is difficult to perform and, as a result, little direct information exists on the exact chemical nature of incinerator fly ash emissions. In order to obtain more specific data on the inorganic compounds present, a group of stack fly ash emissions was collected from both municipal refuse and municipal sludge incinerator operations. After these emissions were analyzed for their cation and anion contents, X-ray diffraction (XRD) and Fourier Transform infrared (FT-IR) techniques were applied for compound identification analyses. These latter analyses showed the presence of many inorganic species in addition to oxides in the fly ashes. The use of the FT-IR technique is detailed in the report, because its application to inorganic species identification is relatively new.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The increasing tonnages of particulate matter emitted to the atmosphere are a serious concern in the field. In past years, waste disposal by incineration lost favor in some municipalities concerned about their inability to meet pending air pollution standards and the concomitant higher operational costs. Also, greater technical skill is required for incinerator operation than for landfill disposal methods. Fortunately, resistance to incineration is lessening because of the magnitude of disposal tonnages, the decreasing availability of landfill sites, and the attraction of energy recovery from waste combustion processes.

Municipal officials charged with the responsibility for waste disposal must know the environmental consequences of incineration, including identification of the chemical nature of the particulate species being emitted. These particulates are principally inorganic fly ashes.

Because methods for inorganic speciation of emission particulates from incineration are limited, time consuming, and technically difficult, inorganic emission constituents are usually determined on the basis of their metal contents only. Frequently, these metal contents are mathematically converted to oxides in order to show an approximate material balance for the fly ash composition; e.g., Si to SiO_2, Al to Al_2O_3. Such arbitrary conversions can be misleading, since the incineration fly ash particulates can have a mixture of origins including:

(1) Mineral residues not destroyed by the brief passage through the flame zone or that bypass the central flame zone.
(2) Molten or solid material formed by condensation of elementary species in the immediate post-flame zone.
(3) Nucleated material from supersaturated vapors in the subsequent cooling zones.
(4) Material added to the existing particulate by physical and/or chemical absorption
(5) Compositions formed by reactions of species in 1 through 4 above.
(6) Physical reconstitution, e.g., crystallization.

Note that in origin 2 (above), the material undergoes rapid temperature change on the order of 2000°F in a few seconds, and there can be a considerable deviation from the equilibrium composition determined thermodynamically. Based on these parameters, fly ashes from the incineration process will consist of a complex mixture of amorphous and crystalline substances.

Inorganic speciation, what little has been done, has relied mostly on X-ray diffraction, morphological characterization of particle groups by microscopy, and, indirectly, by scanning electron transmission and electron microprobe spectroscopy. X-ray diffraction is applicable only to crystalline compounds, and, as in the case of fossil-fuel-combustion fly ash, incineration of waste should result in high concentrations of glassy, amorphous species. Petrographic and other microscopic techniques can look at only small areas and surfaces of samples that are not representative of the total sample. Because of these limitations, the use of Fourier Transform infrared (FT-IR) spectroscopy in this study emphasized identification of inorganic species in fly ash emissions from waste incineration operations.

The primary objective of this research was to identify the inorganic compounds present in fly ash emissions from incineration of municipal refuse and sludge. Due to the high combustion temperature used, these inorganic constituents should represent the major portion (>90 weight percent) of these emissions. Since the application of FT-IR to inorganic compound identification and analysis is relatively new, its use in this program entailed considerable development efforts, including the preparation of additional spectra to the researchers' spectral reference library. These FT-IR development efforts limited the number of samples to which the compound analysis could be applied, principally to three incinerator fly ash samples, two from municipal refuse and one from municipal sludge. These samples were judged representative of the incineration fly ashes based on their elemental contents.

A secondary objective of the program was to obtain data on the elemental (cation/anion) contents of fly ashes emitted from waste incineration operations. Most data given in the literature are for bottom-ash and precipitator-ash contents and not for ashes emitted to the atmosphere. To provide the data needed for this study, six incinerator operations were sampled and analyzed.

Conclusions

Samples of fly ash were collected as particulate matter emitted from the stacks of municipal refuse and municipal sludge incinerators. Based on elemental analyses of these samples and their compound structures, the following conclusions were reached:

(1) The particulate emissions from the incinerators are largely (>90 percent) inorganic in nature.
(2) The particulate emissions are from one-third to one-half water soluble.
(3) The water soluble phase of the municipal refuse incinerator fly ashes is principally chloride and sulfate salts of Na, K, Ca, and Zn, and, to a lesser extent, NH_4^+ salts.
(4) The water soluble phase of the municipal sludge incinerator fly ashes is principally sulfate, and, to a lesser extent, phosphate and chloride salts, also of Na, K, Ca, Zn, and NH_4^+.
(5) The water insoluble phase of the municipal refuse incinerator fly ashes is principally oxide and silicate salts of Al, Si, Ca, Pb, Zn and Fe, plus some insoluble sulfate salts and carbon products.
(6) The water insoluble phase of the municipal sludge incinerator fly ashes is principally oxide, silicate, and phosphate salts of Al, Si, Ca, Pb, Zn and Fe plus insoluble carbon products.
(7) The major differences between the composition of the fly ashes from the two types of incineration processes are the high concentrations of chlorides, derived from plastics in the municipal refuse feed, and the high concentration of phosphates, derived from human and animal wastes in the municipal sludge feed.
(8) With respect to compound identification, the FT-IR technique provided more definitive information than was obtained by X-ray diffraction. Based on the comparatively low intensities of the X-ray patterns, both types of incinerator fly ashes appear to be highly amorphous in nature and, as such, not as amenable to XRD as to FT-IR analysis.

Compositional Analysis

Fly ash samples collected from the stack-sampling ports (beyond any control device) of municipal refuse and municipal sludge incinerator plants were analyzed for their cation/anion contents. As would be expected from the high-temperature combustion processes, the particulate emissions consist principally of inorganic matter including relatively high concentrations of carbon, presumably uncombusted soot. $MeCl_2$ solubility data indicate an approximate total organic fraction of 3 to 7 percent. The analyses showed the fly ash emissions to be from 34 to 47 percent water soluble and weakly acidic in the water extraction solution. The refuse ashes are characterized by high concentrations of $SO_4^{=}$, Cl^-, and low PO_4^{-3}, and NO_3^- contents, whereas the sludge-derived incinerator fly ashes contain high $SO_4^{=}$ and PO_4^{-3} but low Cl^- anions. The NO_3^- and NH_4^+ contents of the sludge fly ashes are higher than those found in the municipal refuse fly ashes, as are many of the heavy metals, especially Cr, Ni, Cu, Ag, Cd, Sn, Pb, and Bi. There are only small differences between the municipal refuse and municipal sludge fly ash types with respect to the concentrations of the major alkali, alkaline earth, and silicon components. The total oxygen contents of the samples were not determined.

Compound Identification

Prior work on coal- and oil-fired power plant fly ash emissions has shown that it is advantageous to analyze the water-insoluble and water-soluble phases of the samples, as well as the total unseparated sample when seeking the compounds present. The insoluble phase should contain the oxides and glass phases of the samples, as well as insoluble sulfate, chloride, nitrate, and any soluble phosphate forms contained in the total samples. Identification of compounds in the separated phases aids in the interpretation of XRD patterns and FT-IR spectra found in the total samples.

X-ray Diffraction Analyses

Two municipal refuse samples and one municipal sludge fly ash sample were analyzed by X-ray diffraction using CuK_a excitation and strip chart recording over 2 θ range from 15 to 70 degrees.

The X-ray diffraction pattern intensities obtained were relatively weak, possibly attributable to a low concentration of crystalline substances in the samples. The qualitative identifications are given in Table 1. In each sample, compounds were identified in the water-insoluble phase which could not be identified in the total sample. The identification of K_2ZnCl_4 was noteworthy. Because little data exist in the literature on this compound, a reference sample was prepared to confirm the pattern. Although the reference was prepared from a solution rather than from a gas-phase state, this identification appears to be reasonably certain.

FT-IR Analyses

The same three samples were analyzed by FT-IR using techniques previously developed for fossil-fuel power plant particulate emissions. Infrared spectra were obtained in the H_2O soluble and H_2O insoluble fractions of the samples both before (unbaked) and after heating at 200°C (baked to remove waters of crystallization and readily volatile components). Our computerized spectral search program was used for the water soluble fraction spectra. Presently, this search program is of substantial use only on sulfate species (mainly on the H_2O soluble fraction in which the sulfates predominate), since the researchers' reference spectra library is primarily composed of sulfate salts. A new technique, that of obtaining second derivative spectra, was used to assist in the data interpretation. The second derivative spectra are useful in resolving a complex peak into its components. This overcomes a major problem in identifying specific compounds in a mixture of similar compounds by determining the exact frequencies of several overlapping bands.

Table 1. XRD Analysis of Refuse and Sludge Fly Ashes

Sample	Compound	PDF #	Pattern Strength
I As Received	Halite (NaCl)	5-628	100
	Anhydrite ($CaSO_4$)	6-226	60
	Quartz (α-SiO_2)	5-490	20
	K_2ZnCl_4	30-1015	20
	$KAl(SO_4)_2$	3-337	20
	Unknown		25
I H_2O Insoluble	Quartz (α-SiO_2)	5-490	100
	Anhydrite ($CaSO_4$)	6-226	60
	Anglesite ($PbSO_4$)	5-577	60
	Magnetite (Fe_3O_4)	19-629	40
	Hematite (α-Fe_2O_3)	13-534	30
	Halite (NaCl)	5-628	10
	Unknown		60
II As Received	Halite (NaCl)	5-628	100
	Quartz (α-SiO_2)	5-490	10
	Anhydrite ($CaSO_4$)	6-226	10
	K_2ZnCl_4	30-1015	10
	Unknown ($MeCl_2$ Soluble)		30
	Unknown ($MeCl_2$ Insoluble)		20
II H_2O Insoluble	Quartz (α-SiO_2)	5-490	100
	Calcite ($CaCO_3$)	5-586	30
	Anhydrite ($CaSO_4$)	6-226	20
	Magnetite (Fe_3O_4)	19-629	15
	Unknown		30
IV As Received	Anhydrite ($CaSO_4$)	6-226	50
	Quartz (α-SiO_2)	5-490	40
	Unknown ($MeCl_2$ Soluble)		100
	Unknown ($MeCl_2$ Insoluble)		70
IV H_2O Insoluble	Quartz (α-SiO_2)	5-490	90
	Unknown		100
V As Received	Calcite ($CaCO_3$)	5-586	50
	Goethite (α-FeOOH)	29-713	40
	$Fe_4(P_2O_7)_3$	24-526	70
	Quartz (α-SiO_2)	5-490	30
	Halite (NaCl)	5-628	30
	Calcite ($CaCO_3$)	5-586	30
	Unknown		20

Summary of Compound Identification

Although IR and XRD data are not in complete agreement, correlations between the two sets of data fit relatively well (see Table 2) when the data from the total, water soluble and water insoluble analyses have been combined. In general, the IR technique gives more total information due to the capability of the IR to provide analyses and speciation of the water soluble to components, the amorphous components, and the organics. The latter capability was not utilized on this program. The incineration fly ash samples do not appear to be highly crystalline. This does not adversely affect the obtaining of IR spectra, but, of course, does limit identification by XRD. XRD, on the other hand, provides information on inorganic chlorides (which give no IR bands) and identifies oxides with more certainty.

From the IR data alone, it is relatively easy to distinguish between types of incineration emission sources (i.e., between refuse and sewage sludge fly ash samples). For example, the sewage sludge fly ash samples contain inorganic P-O compounds and $(NH_4)_2SO_4$ which are found only in very low amounts in the refuse fly ashes.

Both fly ash types contain high quantities (34 to nearly 50 percent) of water soluble components, mostly sulfate, chloride and, in the case of sludge fly ashes, phosphate salts. Obviously, these emissions pose more of an environmental problem than would be encountered if they were of a more chemically inert nature, such as glassy or oxide structures.

The FT-IR technique has been shown in this work and in prior, related studies to be useful for the identification of inorganic species in environmental samples. With a more complete spectral reference library, sulfate, nitrate, oxide and other metal and ammonium salts can be individually identified in samples; in most cases, more completely identified than can be done using XRD. In areas where inorganic compound identification is of concern, such as acid deposition studies, the FT-IR technique should be considered for use, at least as a complement to XRD and other compound-identification techniques.

Table 2. *Identifications Made on Incinerator Fly Ash Samples by IR and XRD*

Sample	*IR Identifications*	*XRD Identifications*
I Municipal refuse fly ash-	$CaSO_4$	$CaSO_4$
	$ZnSO_4$	-
	Na_2SO_4	-
	K_2SO_4	-
	$KAl(SO_4)_2$	$KAl(SO_4)_2$
	-	$PbSO_4$
	-	$NaCl$
	-	K_2ZnCl_4
	SiO_2	SiO_2
	Fe_3O_4	Fe_3O_4
	Al_2O_3	-
	Inorganic unknown	*Inorganic unknown*
	Aliphatic hydrocarbon	-
	Aromatic or olefinic hydrocarbon	-
	Ester carbonyl	-
	Acid carbonyl	
II Municipal refuse fly ash-	$CaSO_4$	$CaSO_4$
	K_2SO_4	-
	$ZnSO_4$	-
	Na_2SO_4	-
	$PbSO_4$	-
	-	$NaCl$
	-	K_2ZnCl_4
	SiO_2	SiO_2
	Fe_3O_4	Fe_3O_4
	Al_2O_3	-
	-	$CaCO_3$
	$XHCO_3$	-
	Inorganic unknown	*Inorganic unknown*
	Aliphatic hydrocarbon	-
	Aromatic or olefinic hydrocarbon	-
	Ester carbonyl	-
	Acid carbonyl	
	-	*Organic unknown*
IV Sewage sludge fly ash -	$(NH_4)_2SO_4$	-
	$CaSO_4$	$CaSO_4$
	$ZnSO_4$	-
	K_2SO_4	-
	Na_2SO_4	-
	$KAl(SO_4)_2$	-
	SiO_2	SiO_2
	Fe_2O_3	-
	$CaHPO_4$ $CaPO_4$ CaP_2O_7	-
	Inorganic unknown	*Inorganic unknown*
	Aliphatic hydrocarbon	-
	Aromatic hydrocarbon	-
	Aromatic ester	-
	Carboxylic acid	-
	Lactone, anhydride, or peroxide	-
	-	*Organic unknown*

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The complete report, entitled "Inorganic Compound Identification of Fly Ash Emissions from Municipal Incinerators," (Order No. PB 83-146 175; Cost: $8.50, subject to change) will be available only from:
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