

Molecular Structure and Microstructure of Primary PM_{2.5} Derived from the Combustion of Coal and Residual Oil

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Summary

There is much need to increase our knowledge concerning the occurrence of key metallic elements in particulate matter (PM) derived from combustion sources. Recent evidence increasingly supports the proposition that metals in fine airborne PM are associated with adverse health effects. Furthermore, the concentrations of metallic elements in primary PM samples are used as input to chemical mass balance models for apportioning the contribution of various sources of PM to ambient PM. Despite these major roles in both health-effect and source apportionment studies of PM, there have been relatively few studies aimed at determining precisely how metals do occur in PM samples.

In this work, X-ray absorption fine structure (XAFS) spectroscopy, complemented by other techniques such as computer-controlled scanning electron microscopy (CCSEM), transmission electron microscopy (TEM), and iron Mössbauer spectroscopy, are being employed to characterize primary particulate matter samples derived from the combustion of seven coals and four residual oils. Determination of the speciation of key elements (S, V, Cr, Fe, Ni, Zn, As, etc.) in PM and characterization of the microstructure of PM have been emphasized to date. The PM samples were obtained from laboratory-scale combustion experiments that simulate commercial operating conditions. A cyclone separator was used to separate the PM into fractions $>2.5 \mu\text{m}$ (PM_{2.5+}) and $<2.5 \mu\text{m}$ (PM_{2.5}) in size. In addition, leaching experiments have been performed on the separated PM fractions to aid identification of soluble and insoluble elemental occurrences.

For the PM samples derived from residual oil fly ash (ROFA) produced in a small institutional fire-tube boiler, unburned carbon char was the principal constituent (~65% to 98% by mass). This fact reflects the inherently low ash contents of the residual fuel oils (0.02 to 0.10% by mass) and the high heat transfer and flue gas quenching rates associated with this boiler design. In the ROFA PM from this boiler, the metals varied in concentration from as much as 5.8 wt% for vanadium in PM from high sulfur residual oils to less than 1 ppm. In most cases, the concentration of the metal was significantly higher in the finer PM_{2.5} fraction than in the corresponding PM_{2.5+} fraction. XAFS spectroscopy established that in addition to sulfur as sulfate, which was the dominant sulfur form, sulfur also occurred in organic sulfur (as thiophene derivatives), elemental sulfur and sulfide forms. The thiophene sulfur forms comprised between 30 and 40% of the total sulfur in the PM_{2.5+} samples, but lesser amounts in the PM_{2.5} samples, and clearly mirrored the fraction of unburned carbon in the PM samples. XAFS spectroscopy also showed that most of the metals were present as sulfates and several specific sulfate were identified, including VOSO₄.xH₂O, NiSO₄.xH₂O, PbSO₄, and ZnSO₄.xH₂O. However, additional metal species were also encountered, including Cu(NO₃)₂.xH₂O, NiFe₂O₄, Ni₃S₂, Fe_{1-x}S, and CuS. The sulfide samples, including the potentially carcinogenic nickel subsulfide, were more prevalent in the coarser PM_{2.5+} fractions and were readily identified in the residues from the aqueous leaching experiments, which removed most of the sulfate forms.

In contrast, one PM_{2.5} sample prepared in a refractory-lined combustor had essentially no carbon content, much higher contents of metals (up to 13.6 wt% V), and a much finer particle size distribution. The residual oil was clearly much more completely combusted in this furnace. For this sample, XAFS spectroscopy indicated that essentially all of the sulfur was

present in the form of sulfate and that no metal sulfide was present. Minor differences in the appearance of the XANES spectra for some of the metals were noted in comparison with those from the PM_{2.5} samples from the fire-tube boiler.

For the PM samples derived from coal combustion, unburned carbon contents were much lower and did not exceed 20% in any sample. XAFS spectroscopy showed that sulfate was also the dominant form of sulfur in coal PM, with minor amounts of thiophenic and elemental sulfur forms present. In addition, certain PM samples derived from combustion of western coals exhibited minor fractions of their sulfur as sulfite. Arsenic was found to exist in the coal-derived PM exclusively in the As⁵⁺ oxidation state; no evidence was seen for the presence of the more toxic As³⁺ oxidation state. Chromium was observed to be exclusively present as Cr³⁺ in PM derived from eastern bituminous coals, but PM from western coals contained up to 30% of the chromium in the more toxic and carcinogenic Cr⁶⁺ oxidation state. Zinc exhibited a characteristic XAFS spectrum for eastern bituminous coals that derives principally from zinc in the spinel phase, Zn(Fe,Al)₂O₄. The speciation of zinc in PM from western coals is different and more complex. Iron Mössbauer spectroscopy indicated that the average oxidation state of iron was higher for the PM_{2.5} fraction than for the corresponding PM_{2.5+} fraction, indicating that the smaller PM particles are always more oxidized than the larger particles.

Particle size distributions and chemical composition ranges of the PM from both ROFA and coal fly-ash were investigated by CCSEM and individual particles have been examined by TEM. The microstructure of the coal PM was dominated by spherical and rounded aluminosilicate glass particles that contained significant amounts of Ca in PM from western coals and Fe and K in PM from eastern coals. For ROFA PM, the most interesting microstructure consisted of small metal sulfate particles on the surfaces of larger, highly vesiculated carbon-rich particles.

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