

SIZE DISTRIBUTION OF ASH PARTICLES FORMED DURING COMBUSTION OF  
LOW-SULFUR RESIDUAL FUEL OIL IN AN ELECTRIC UTILITY BOILER

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INTRODUCTION

The size distribution of particulate matter was measured by Piper and Nazimowitz (1985) in Unit 110 at the 59th Street Station of the Consolidated Edison Co. of New York, while firing low-sulfur residual fuel oil. The particles were collected using a low pressure cascade impactor placed in the flue gas at the stack breeching, where the gas temperature was 450 K (350°F). As shown in Figure 1 the particle size distribution has three distinct modes, thought to correspond to the following types of particles, from largest to smallest: 1. Unburned residues of coke formed on loss of volatile matter from spray droplets, 2. Residues of ash left on burnout of coke particles and fragments, 3. Submicron ash particles formed by vaporization of metal atoms and metal oxides from burning coke, followed by nucleation, condensation, and coagulation of the vapor. Because of the high temperature at the sampling location, sulfate was not expected to have been a significant fraction of the particulate matter. Also, because of the long residence time in the unit and high excess oxygen, soot is not expected to have been a major contributor to the submicron particles. The problem is to relate the size distribution and concentration of ash and unburned coke to fuel properties and combustion conditions.

The yield and size of coke particles formed in a boiler flame are considered by McElroy et al. (1992) and Urban, Huey, and Dryer (1992). Calculations of the emission of unburned coke and its size distribution are described by Walsh, Olen, and Washington (1992) and Walsh, Mormile, and Piper (1992). In the present preprint we focus on the two peaks associated with ash, at the left and near the center of Figure 1.

SUBMICROMETER ASH

There are two principal problems associated with a calculation of the size distribution of particles formed from the inorganic matter which vaporizes: determination of the amount of ash vaporized, and calculation of the sizes of particles resulting from coagulation of the fine particles formed on nucleation and condensation of the vapor. A previous paper (Walsh, Mormile, and Piper, 1992) describes the application of the models of Senior and Flagan (1982) and Helble, Neville, and Sarofim (1988) to the latter process. The principal features of that model are as follows: Metal atoms, suboxides, and/or oxides vaporize from burning coke particles and diffuse from the high temperature, reducing atmosphere at the coke surface toward the more oxidizing free stream. The vapor species nucleate and condense as they

move outward, in a sequence determined by their concentrations, the oxygen concentration profile in the boundary layer, the rate coefficients for oxidation of reduced species, and their vapor pressures at the surfaces of the resulting particles (Graham, 1990; Graham et al., 1990). Once particles are formed, diffusion toward the free stream is much slower. The primary mechanism for transport of the particles then becomes the slow outward flow due to the change in gas volume accompanying the reaction  $2C + O_2 \rightarrow 2CO$  at the coke particle surface (Senior and Flagan, 1982). Concentration of ash particles in the coke particle boundary layer explains the large sizes of ash particles ( $\sim 0.2 \mu\text{m}$ ) formed during the short time available. Coagulation occurs in the boundary layer until it dissipates on burnout of the coke, after which coagulation continues at a slower rate in the free stream. The geometric standard deviation of the size distribution formed by coagulation is given by Lee and coworkers (1983, 1984). The process is shown in Figure 2.

The other component of the submicron ash problem is the explanation of the extent of ash vaporization. The model of Quann and Sarofim (1982) and Senior and Flagan (1985) was adapted to vaporization of inorganic species from residual oil coke. The low sulfur oil contained very little vanadium, so the vaporizing species was assumed to be  $\text{SiO}$  formed by reduction of  $\text{SiO}_2$  from aluminosilicate droplets imbedded in the coke. These droplets are derived from particles suspended in the fuel oil, which become incorporated in the coke residues. The aluminosilicate inclusions were assumed to be  $1 \mu\text{m}$  in diameter. The fraction of ash vaporized was calculated for coke particles burning at constant size with decreasing density. Voidage was assumed to be uniform throughout the burning particles, and to increase linearly with time up to the porosity at which the coke disintegrates (Kerstein and Niksa, 1985). The effective pore diffusion coefficient was estimated from the porosity (Holmes, Purvis, and Street, 1990). The vapor pressure of metal suboxide adjacent to the aluminosilicate inclusions was adjusted to reproduce the observed segregation of ash between submicron particles and micron-size residues. The value giving the best agreement with the measurements was  $2.8 \times 10^{-5}$  atm.

The fraction of ash vaporized from small coke particles was limited by the burnout time, while the fraction vaporized from large particles was limited by diffusion. The maximum fraction vaporized occurred at a coke particle size of  $40 \mu\text{m}$ , near the median size of coke formed from the oil spray droplets. For the low ash, low sulfur oils and conditions in the postflame region of the boiler, a typical fraction vaporized was 80 wt% of the ash in the oil. The calculated size distribution of submicron particles is compared with the measured distribution in Figure 1.

#### ASH RESIDUES

Disintegration of the coke particles on approach to complete burnout was assumed to determine the size distribution of ash remaining unvaporized. In order for this to be a good approximation, the ash particles must be uniformly distributed and smaller than the coke fragments. The breakup of coke was assumed to generate a power law distribution of fragments having a number-based probability density proportional to the  $-3$  power of particle size (Holve, 1986; Quann and Sarofim, 1986; Baxter, 1992). This is equivalent to a uniform distribution on a mass basis. Under this assumption, fragmentation of a given size of parent coke particles produces the same mass of fragments in every geometrically-spaced size bin from the minimum fragment size up to the parent particle size. The size distribution of

ash residues left when the fragments burn out is similar to the fragment size distribution, but shifted to smaller sizes by a factor depending upon the initial ash content of the coke and fraction vaporized. The process is shown in Figure 2. All fragments, regardless of their parent particle size, were assumed to have lost the same fraction of ash by vaporization. The minimum size of fragments was adjusted to make the resulting ash residue distribution match the observed particle size distribution in the 0.8 to 7  $\mu\text{m}$  size range. A minimum fragment size of 6  $\mu\text{m}$  gave the best overall agreement with the size distribution measurements.

The calculated distribution of ash residues is shown near the middle of Figure 1. The step on the left side of the peak is the result of the assignment of a specific value (6  $\mu\text{m}$ ) to the minimum size of coke fragments. The shape could be improved by allowing for variation in the amount of ash remaining unvaporized in fragments derived from different sizes of coke particles, or by introducing a more detailed treatment of influences on the fragment size distribution (Miccio and Salatino, 1992).

#### CONCLUSION

The fraction of ash appearing as submicron particles in the products from combustion of a low sulfur residual oil is consistent with the model of Quann and Sarofim (1982) for vaporization of mineral particles imbedded in porous coke, accompanied by diffusion of the vapor through pores to the external surface. The sizes of the particles formed from the vapor are in agreement with the model of Senior and Flagan (1982) for coagulation of submicron particles in the boundary layer of a burning char particle.

The sizes of residues formed by the ash remaining unvaporized in the coke were assumed to depend upon the sizes of fragments formed on disintegration of the coke. The assumption of a uniform mass-based size distribution for the fragments, and a minimum fragment size of 6  $\mu\text{m}$ , produced a distribution of micron-size ash particles similar to measurements in the 1 to 10  $\mu\text{m}$  range, using a cascade impactor.

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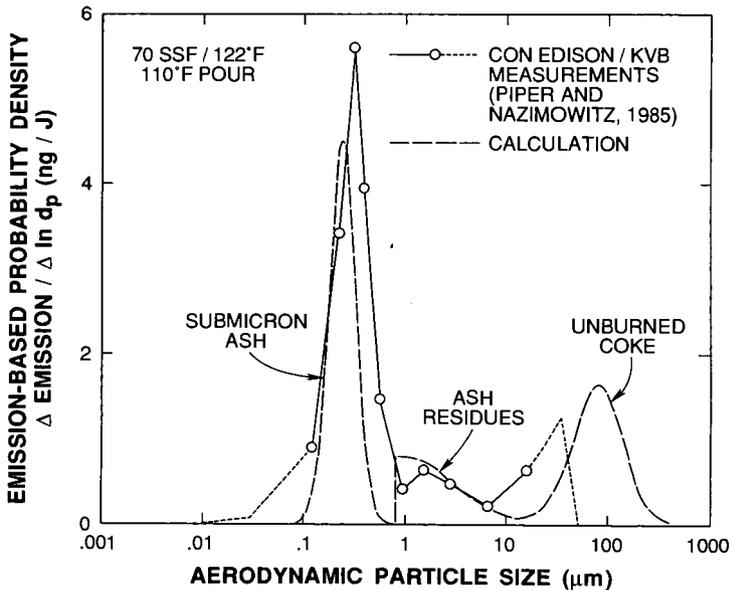


Figure 1. Emission-based size distribution of particles collected at the stack breaching in Unit 110 of the Consolidated Edison Co. of New York, using a low pressure cascade impactor (Piper and Nazimowitz, 1985). The fuel was residual oil containing (wt %): 86.64 carbon, 12.39 hydrogen, 0.23 nitrogen, 0.29 sulfur, 0.37 oxygen, 0.02 ash, 0.5 asphaltenes (IP 143), and 12 wt ppm vanadium. The API gravity was 21.3, heating value was 44.1 MJ/kg, viscosity was 70 SSF at 50°C, and the pour point was 43°C. The excess oxygen in flue gas was 2.4 mol %.

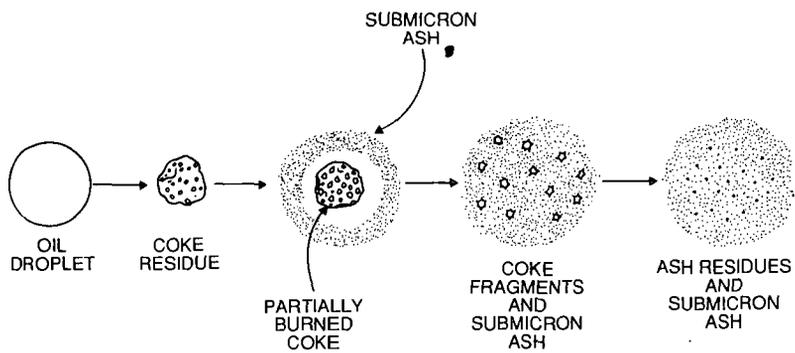


Figure 2. Formation of submicron ash and ash residues during combustion of residual oil coke particles.