

## DEPENDENCE OF PARTICULATE MATTER EMISSIONS FROM BOILERS ON QUALITY OF RESIDUAL FUEL OIL

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### INTRODUCTION

In a recent paper, Walsh, Wei, Mormile, Piper, Olen, and Washington (1991) outlined an approach to the estimation of concentrations and size distributions of ash and unburned coke particles in flue gas from residual oil-fired electric utility boilers. Three contributions to particulate matter were considered: unburned coke, submicrometer ash formed from vapor, and ash residues left on burnout of coke. Other components of particulate, such as sulfate and soot, were not included. More detailed methods for calculating the concentrations and size distributions of unburned coke, submicrometer ash, and ash residues have been developed, as described below.

Size distributions of stack particulate were measured by Piper and Nazimowitz (1985) during combustion of 0.3 wt% sulfur oils in a 62 MW boiler of the Consolidated Edison Co. of New York. Samples were collected at the stack breeching, where gas temperature was 450 K (350°F). A representative size distribution, with indications of the materials thought to be the principal contributors to each of the three modes, is shown in Figure 1. The proposed mechanism for formation of the particles is presented in Figure 2.

### RESULTS AND DISCUSSION

#### Unburned Coke

Under normal conditions, about 99% of the coke formed in a residual oil spray flame burns out in the furnace. The few particles which survive, do so because of extreme properties or conditions under which they make their passage through the furnace: large particle size, low reactivity, short residence time, low temperature, or rich mixture. A large part of the difficulty in simulating the process arises from the need to account for the nonuniformity of particle properties and furnace conditions.

A detailed analysis of factors controlling the combustion of petroleum coke was recently given by Stanmore (1991). For the present simulation of coke combustion in a boiler, coke residues were assumed to burn at constant size with decreasing density, according to a reaction which is first order with respect to oxygen concentration, producing carbon monoxide which burns far from the particle surface. Each particle was assumed to remain at its initial size until it disintegrated, at the critical porosity (Kerstein and Niksa, 1985). The fragments were assumed to burn instantaneously. The mean temperature was estimated from the furnace exit gas and adiabatic flame temperatures (Hotel and Sarofim, 1967). Particles and gas were assumed to be at the same temperature. Allowance was made for a distribution of residence times in the furnace (Beér and Lee, 1965).

The present calculation differs from the previous one (Walsh et al., 1991) in its consideration of a distribution of oxygen concentrations, arising from uneven distribution of fuel and air among the burners (Lawn and Godridge, 1987), from fluctuations in fuel and air flowrates, or from imperfect mixing of spray droplets with combustion air. The calculation was done by separating the gas/particle flow into two imaginary streams, one rich and one lean, whose average oxygen content is that which would be present in a perfectly mixed postflame region, after combustion of volatiles. The difference between the oxygen content of either stream and the average is the standard deviation of the oxygen concentration distribution at the onset of coke combustion. The concentration in both streams decays exponentially toward the flue gas excess oxygen as the streams are mixed. When the initial O<sub>2</sub> content of the rich stream was less than zero, no combustion of coke was allowed until mixing with lean gas raised its oxygen content above zero. Both the standard deviation of the initial oxygen concentration distribution and the characteristic mixing time were adjusted to fit the unburned carbon emission measurement, but the two values together were constrained by the observed O<sub>2</sub> distribution in flue gas, determined by a traverse at the economizer outlet. The mixing time is characteristic of the postflame flow, rather than the jet-stirred region near the burners.

The probability density function for the aerodynamic sizes of coke particles surviving at the furnace exit was obtained by integration of the contributions to each size of unburned particles from all sizes of coke particles formed in the flame. Values of the parameters having the greatest influence on the coke particle size distribution are given in Table 1. The size distributions of particles remaining unburned are shown on the right hand side of Figure 1 (peak labeled "unburned coke"). When compared with the earlier result (Walsh et al., 1991), one sees that the introduction of the oxygen concentration distribution allows smaller particles to survive, improving the agreement between model and measurements. However, the calculated sizes are still two to three times larger than observed. Two possible approaches to reconciling this discrepancy might be to account for size reduction during burnout and to allow for a distribution of furnace temperatures.

### Ash Residues of Coke Fragments

Vaporized ash forms submicrometer particles, while the nonvaporized ash forms micrometer-sized residues. The extent of vaporization is expected to depend upon ash composition, temperature, oxygen concentration, and the structure of the coke (Quann and Sarofim, 1982; Senior and Flagan, 1985). We have not attempted to simulate the vaporization process, so the fraction vaporized was simply adjusted until the calculation reproduced the heights of the submicron and residue peaks.

The breakup of coke particles during burnout divides the ash retained in the coke among smaller fragments. If inorganic species were uniformly distributed through the coke, the size distribution of fragments would determine the sizes of ash residues formed when the coke burns out (Flagan, 1979; Kang et al., 1989). In the previous calculation (Walsh et al., 1991), the mean size of fragments was derived from measurements of the sizes of partially burned coke (Lawn et al., 1987). A different approach was taken here.

The cumulative mass-based fragment size distribution was assumed to take the form of a power law (Kerstein and Niksa, 1985):  $F(d_f) = (d_f/d_C)^n$ , in which  $d_f$  and  $d_C$  are the sizes of fragments and parent coke particle, respectively. The probability density function for the fragments was obtained by integration of the contributions to a given size from all sizes of parent particles. The exponent,  $n$ , was assigned the smallest value thought to be reasonable ( $n = 1$ ), which implies a uniform distribution (by mass) of fragments formed from each size of particle. The ratio of ash residue size to fragment size is obtained from the ash content of the oil, the coke yield in the flame, and the densities of ash and coke. The result is shown in Figure 1 (peak labeled "ash residues"). The most probable size of residue in the calculated distribution is five times larger than that obtained in the previous calculation (Walsh et al., 1991), and about four times larger than the size at the peak in the measurements (at  $\sim 1 \mu\text{m}$ ).

Although this calculation provides an explanation for the presence of particles having sizes in the range from 0.6 to 7  $\mu\text{m}$  in the flue gas, there is not a satisfactory fundamental basis for the calculation of the coke fragment size distribution. Some measurements and analysis of the breakup of residual oil coke particles are needed. The spherical macropores in the coke are expected to have an important effect on the fragment size distribution (Kerstein and Niksa, 1985; Kang et al., 1989). The ash residue sizes may also be influenced by the sizes of inorganic particles (e.g. fluidized catalytic cracker fines and MgO) in the oil, which become incorporated in the coke.

### Submicrometer Ash

Ash not assigned to the residues was assumed to vaporize during combustion of coke. Oxidation and cooling in a coke particle boundary layer cause supersaturation of the vapor. Nuclei formed from the vapor grow by condensation until the condensable species are depleted, after which growth continues by coagulation of the particles. The ultimate particle size distribution, after the relatively long residence times characteristic of combustion, is determined primarily by coagulation (Friedlander, 1977; Flagan, 1979; Neville et al., 1981).

The key to a satisfactory calculation of the most probable size of submicron particles was provided by the work of Senior and Flagan (1982, 1985) and Helble, Neville, and Sarofim (1988). Senior and Flagan (1982) pointed out that the principal mechanism for transport of submicron ash particles away from their parent coke or char particle is the convective flow arising from the increase in gas volume accompanying the reaction  $2\text{C} + \text{O}_2 = 2\text{CO}$  at the coke particle surface. Because the volume fraction of submicron particles in the coke particle boundary layer is 200 times greater than after uniform mixing in the free stream, most of the coagulation and size increase occur in the vicinity of the coke. Helble et al. (1988) reached similar conclusions from consideration of convection and diffusion, when the coke particle is moving relative to the ambient gas.

In the present calculation it was assumed that submicron particles are confined to the outward flow from a coke particle as long as it is burning, but that the submicron particles

become uniformly mixed at the instant the coke burns out. Increase in size by coagulation of the well-mixed particles could not be neglected, since the mean residence time in the furnace and convective sections is 50 times longer than the burning time of the mean size of coke. A refinement of this approach, considering details of the mixing process, would be possible using the theory of Heible et al. (1988).

The average of Lee and coworkers' results for the geometric standard deviation of the sizes of coagulated aerosols formed in the continuum (Lee, 1983) and free molecule (Lee, Chen, and Gieseke, 1984) regimes was used to calculate the particle size distribution shown in Figure 1 (peak labeled "submicron ash"). In calculating the aerodynamic diameters, corrections were made for both density and the change in Cunningham correction for slip (Flagan and Seinfeld, 1988). However, the effect of the particles' not being spherical (Ulrich and Subramanian, 1977; Graham et al., 1990) was not considered. The calculated mean aerodynamic particle size was approximately 0.2  $\mu\text{m}$ , compared with the peak in the measurements at 0.3  $\mu\text{m}$ . This is a marked improvement over the previous calculation (Walsh et al., 1991), in which the coagulating particles were assumed to be uniformly mixed with gaseous combustion products.

#### Effects of Fuel Quality

The primary influence on unburned coke is the mass fraction of fuel converted to coke. There are two effects of increasing the coke yield: 1. The amount of coke to be burned increases, and 2. Particle size increases, although weakly [size is proportional to the one-third to one-half power of coke yield (Urban and Dryer, 1990b, 1991)]. Our estimate of coke yield was based on the IP 143 asphaltene analysis (Lawn et al., 1987; Holmes, 1989; Olen, 1989; Urban and Dryer, 1990a). An apparatus for the measurement of coke formation, under conditions simulating pyrolysis in a flame, is under development for routine analysis of fuel oils (McElroy, Muzio, and Carl, 1991).

Coke particle sizes depend upon the fineness of the spray, which depends upon the viscosity of oil in the atomizing tip. It is often assumed that the required temperature for a desired viscosity can be obtained from a universal viscosity-temperature relationship for fuel oils. However, there is significant variation in temperature dependence of viscosity among residual oils (Olen, 1988). Agglomerated asphaltene may influence atomization behavior (Audibert, 1989).

The ash content of fuel oil determines the total of submicron ash and ash residue contributions to particulate matter, which, for the fuel and boiler under consideration, was approximately the amount of material smaller than 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ). To make useful calculations of collection efficiency and opacity one would require, in addition, an estimate of the proportions of vaporized ash and residues. The Consolidated Edison Co. of New York measurements indicated that the fraction of ash vaporized was 30 to 80 wt%, much greater than during pulverized coal combustion, and the fraction vaporized was not well correlated with  $\text{NO}_x$  emission (McElroy, Carr, Ensor, and Markowski, 1982). Experience in the field shows that submicron ash increases with increasing vanadium in the oil (Walsh, Olen, Mormile, and Piper, 1990). Particles suspended in the oil (FCC catalyst,  $\text{MgO}$ ) are expected to contribute to 1 to 10  $\mu\text{m}$  residues.

We have not included discussion of the important contributions of sulfate to particulate matter and sulfuric acid mist to stack plume opacity, because the samples under consideration were collected from flue gas at temperatures well above the acid dewpoint.

Sulfate and acid mist depend upon the sulfur, vanadium, and sodium contents of the oil, MgO treatment, and the extent to which excess air can be lowered without causing unacceptable unburned carbon emission.

## CONCLUSIONS

Agreement between calculated and observed size distributions of unburned coke in flue gas was improved by the introduction of a fuel/air ratio distribution at the burners, which enabled smaller particles to remain unburned at the furnace exit. It appears, however, that allowance for particle size changes during burnout and the distribution of furnace temperatures may be needed to further improve the calculation of the size distribution of unburned particles.

Intermediate-size particles, in the range of aerodynamic sizes from 0.6 to 7  $\mu\text{m}$ , were thought to be ash residues left on burnout of coke fragments. The assumption of a uniform distribution of fragment sizes formed from each size of parent coke particles roughly imitated the observed size distribution in this range. A better analysis is needed for the fragmentation behavior of particles having the structure of residual oil coke.

The growth of submicron particles by coagulation following nucleation and condensation of vapor-phase inorganic species was simulated by dividing the process into two stages. In the first stage, particles were confined to the convective flow from the coke surface, driven by combustion of the coke (Senior and Flagan, 1982). In the second stage, following burnout of the coke, the submicron particles were uniformly mixed with combustion products. High concentration of particles is characteristic of the first stage, while long residence time is characteristic of the second. The mean size of particles obtained from this calculation was in good agreement with the most probable size in the submicron peak of the measured distribution. The most important limitation on the predictive capability of this calculation is the lack of a model for vaporization of ash, which would describe the segregation of ash between residues and submicron particles.

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Table 1. Values of parameters used in the calculation of the particle size distribution.

| Parameter  | Value                        | Source                            |
|--|------------------------------|-----------------------------------|
| Furnace volume   | 2088 m <sup>3</sup>          | furnace dimensions                |
| Furnace plan area  | 91 m <sup>2</sup>            | furnace dimensions                |
| Distance from burners to furnace exit  | 16.3 m                       | furnace dimensions                |
| Load   | 62 MW                        | Piper and Nazimowitz (1985)       |
| Furnace exit gas temperature   | 1480 K                       | typical                           |
| Mass median spray droplet size   | 120 μm                       | Wigg (1964)                       |
| Geometric standard deviation of the droplet size distribution                    | 1.83                         | Simmons (1977)                    |
| Mass fraction of fuel oil converted to coke                                      | 0.22(IPA/100) <sup>0.4</sup> | Olen (1989), Holmes (1989)*       |
| Apparent density of coke   | 690 kg/m <sup>3</sup>        | Lawn et al. (1987)                |
| Dimensionless standard deviation of the oxygen concentration distribution        | 1                            | adjusted                          |
| Characteristic time for mixing in the postflame region                           | 1.2 s                        | adjusted                          |
| Exponent in power law describing the coke fragment size distribution             | 1                            | adjusted                          |
| Sticking propability in collisions between submicrometer particles               | 1                            | assumed                           |
| Geometric standard deviation of the submicrometer ash particle size distribution | 1.34                         | Lee (1983)<br>Lee et al. (1984)   |
| Apparent density of ash  | 2500 kg/m <sup>3</sup>       | typical of aluminosilicates       |
| Average temperature during coagulation in the convective section                 | 1000 K                       | average of furnace exit and stack |
| Total residence time in furnace and convective sections                          | 10 s                         | estimate                          |
| Fraction of ash vaporized  | 60 wt%                       | adjusted                          |

\*IPA = IP 143 asphaltenes (wt %).

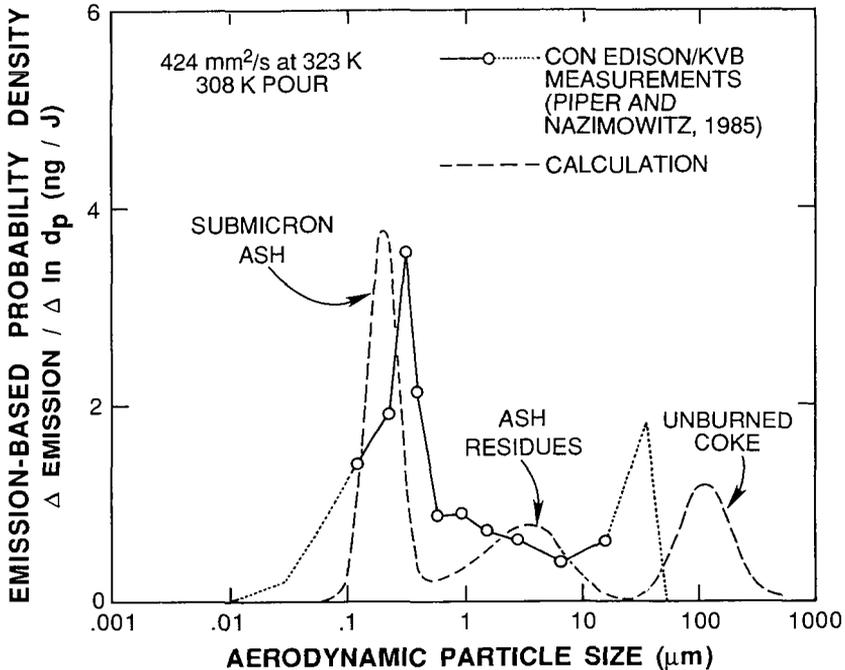


Figure 1. Emission-based size distribution of particles separated from flue gas at the stack breaching in Unit 110 at the 59th Street Station of the Consolidated Edison Co. of New York (Piper and Nazimowitz, 1985). The fuel oil properties were: viscosity at 323 K (122°F), 424 mm<sup>2</sup>/s (200 SSU); pour point, 308 K (95°F); sulfur, 0.29 wt%; ash, 0.02 wt%; IP 143 asphaltenes, 1.6 wt%; and vanadium, <10 wt ppm. The excess oxygen in flue gas was 3.1 mol%. The extreme left and right portions of the experimental curves are shown dotted, to indicate that the shape in these regions depends upon the maximum and minimum sizes assumed for the particles in the preseparator and final filter, respectively, of the cascade impactor. Although resolution of particle size in these samples might change the shapes of the curves, it would not change their areas. The dashed curve is the result of the calculation described in the text.

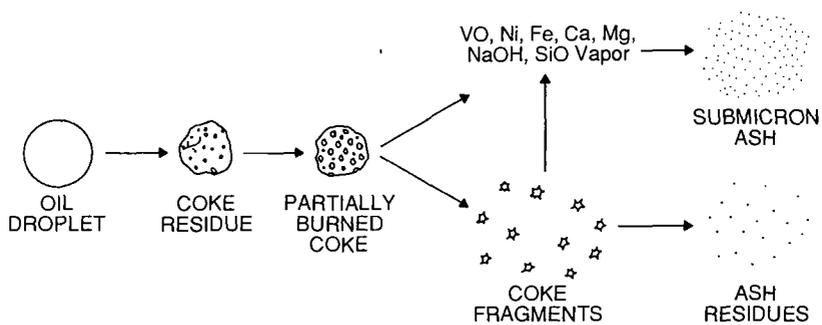


Figure 2. Mechanism for formation of particles observed in flue gas, in the absence of soot, and while temperature is still above the sulfuric acid dewpoint. Under these conditions the principal components of particulate matter are thought to be partially burned coke residues, ash residues remaining on burnout of coke fragments, and submicrometer ash formed by nucleation, condensation, and coagulation of vaporized inorganic species. Typical sizes are: oil droplets (mean), 100 to 200  $\mu\text{m}$ , unburned coke, 10 to 300  $\mu\text{m}$ , ash residues, 0.5 to 8  $\mu\text{m}$ , and submicrometer ash, 0.1 to 0.5  $\mu\text{m}$ .