Combustion Fume Structure and Dynamics

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1 Introduction

During pulverized coal combustion, a fume of submicron particles is formed from the mineral matter in the parent coal. Studies of the variation in chemical composition with particle size have revealed that much of the submicron fume is formed from volatilized coal ash [1, 2, 3]. The formation and evolution of the ash fume is governed by homogeneous nucleation, condensation, and coagulation. Vapors of refractory species nucleate relatively early in the combustion process. Coagulation of those fine particles results in a size distribution that is approximately log normal. More volatile species remain in the gas phase until after the nucleation has taken place. Condensation on the surfaces of both the fume and the larger residual ash particles results in the enrichment of the fine particles with volatile, and frequently toxic trace species. The resultant concentration of heavy metals in the size interval between 0.1 and 1 μm may allow disproportionate amounts of these species to escape collection, even by the best of gas cleaning systems.

Flagan and Friedlander [1] first modeled the evolution of the ash particle size distribution in pulverized coal combustion beginning with the hypothesis that the fine particles resulted from homogeneous nucleation and grew primarily by coagulation. They predicted much more distinct peaks in the submicron size range than had been observed at that time. Improved instrumentation has verified those predictions, and shown that the situation can be even more complex than their simple model indicated. In some cases multiple peaks are seen in the size distribution of the submicron fume particles [4]. This could occur relatively late in the cooling of the combustion products when a second vapor becomes sufficiently supersaturated to undergo homogeneous nucleation in spite of the large numbers of fume particles produced in the initial nucleation burst. If heavy metals are responsible for this additional nucleation event or if it occurs before the heavy metals condense, further enrichment of the fine particles with heavy metals could result.

A comprehensive theoretical treatment of the aerosol dynamics of pyrogenous fumes requires a number of extensions of the classical descriptions. Rigorous descriptions of the coagulation of dense, spherical particles are available [5, 6, 7], but fume particles are rarely spherical. The materials involved tend to be refractory, so high temperatures are required to achieve complete coalescence. Flame temperatures may be hot enough to melt some materials, so coalescence is not always achieved. Even with systems that can melt the particles in the primary reaction zone, coagulation during the cooling or quench process can form agglomerates. To predict the dynamics of the fumes produced when coalescence is rate limiting, the structure and dynamics of the resulting aggregates must be understood.

Pyrogenous fumes, including soot, coal ash, and synthetic fumes (TiO_2, SiO_2, etc.) exhibit a common structure, namely agglomerates of approximately equiaxed particles (spherules)

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with sizes of a few tens of nanometers. This common structure has been attributed to the physical process of agglomeration [8]. The densities of pyrogenous fume agglomerates decrease with increasing size. Forrest and Witten observed that the aggregate mass varies as a power law of the size of that aggregate, i.e.,

$$m \propto r^D \tag{1}$$

where D has been called the fractal dimension which generally has a value below the Euclidean dimension of 3. Pyrogenous fumes typically have fractal dimensions below 2.

Computer simulations of aggregate formation yield similar structures and provide insights into the formation mechanisms [9]. Relatively dense particles ($D \sim 2.4$) are produced when individual spheres diffuse to the surface of the growing aggregate (diffusion limited aggregation, DLA). Lower density aggregates ($D \sim 1.8$) result from coagulation of like-sized aggregates (cluster-cluster aggregation, CCA). Hence, the simulations suggest that pyrogenous fumes grow by the CCA mechanism. These structure calculations make one very important assumption that is not valid for pyrogenous fumes, namely that the structure of the aggregate does change due to fusion spherules under the driving force of surface tension. This may be expected to increase the fractal dimension of the aggregates as they age, although direct measurements of this effect are still lacking.

Most diffusion limited aggregation and cluster-cluster aggregation models have focussed on the structure of the particle, primarily through computer simulations that employed simplistic models of particle aerodynamics and collision cross sections, usually modeling the particle transport with either continuum or free molecular regime descriptions. Pyrogenous fume particles are frequently comparable to the mean free path of the gas molecules in size, so neither continuum nor kinetic regime models are strictly valid. Direct measurement of aerodynamic parameters for aggregate particles is a prerequisite for the development of a more rigorous understanding of such aerosol systems. To understand the distribution of volatilized trace elements with respect to particle size, it is further necessary to elucidate the mechanisms of mass transport to the surfaces of transition regime aerosol aggregates.

This project comprises theoretical and experimental investigations of the structures and aerodynamics of aggregate pyrogenous fume particles in which the particles are modeled as fractal agglomerates. The objective of this study is to develop and validate a model describing the formation and evolution of fine particles from minerals volatilized during coal combustion,. with special emphasis on particle structure and its influence on the dynamics of the combustion aerosol. The basic approach of this project is to employ fractal structure models to characterize the aggregate particles and to develop models of particle dynamics. The dynamics of the aerosol are simulated using the so-called sectional representation of the particle size distribution. Experimental investigations of the individual processes involved in the aerosol evolution, i.e., sintering and aggregation are studied independently using model systems.

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2 Studies of Structural Rearrangements of Aggregate Particles

Aggregate particle coalescence rates must also be understood if quantitative models of combustion fume evolution are to be developed. An experimental investigation of the sintering rates of aggregate particles was undertaken to develop a data base on the nature of the structural rearrangements and their rates for well defined model materials. Dense spheres of refractory materials were produced by high temperature consolidation of particles produced from volatile precursors. While still entrained in the carrier gas flow, the spherical particles were then allowed to aggregate at low temperatures to form doublets or bispheres. Finally, the bispheres were heat treated in a second flow reactor at controlled temperatures and residence times to induce sintering. Particles at various stages of densification were collected and analyzed using transmission electron microscopy. Extensive experimental studies of the bisphere agglomerates were conducted to provide a database for testing models of agglomerate sintering.

In the previous reporting period, we reported on experimental observations of the sintering of idealized aerosol agglomerates of elemental silicon. The initial experiments yielded some most perplexing results. Under conditions that led to complete coalescence of the bispheres, aggregate particles did not coalesce. After extensive investigation, it was concluded that the surfaces of the aggregate particles were contaminated with an oxide layer. The DMA classifies charged particles by drifting them across a particle free sheath flow in the presence of an electric field. The sheath flow rate is an order of magnitude larger than either the aerosol flow entering the instrument or the classified aerosol flow leaving the instrument. The precision of the measurement depends on the measurement of three flows and the determination of a fourth small flow by difference. In order to obtain the required precision in control of the four flows of the DMA, the sheath air was recirculated through a sealed diaphragm pump. Very minor air leakage in the recirculation system was sufficient to contaminate the surfaces and alter the sintering properties. The recirculation system has been eliminated from the apparatus, and additional flow metering has been provided to prevent this contamination. With these changes, agglomerate particles were found to sinter as expected.

During this reporting period, studies of the structural rearrangements of agglomerate particles emphasized: (i) electron microscopic examination of the many samples of size classified agglomerate particles at various stages of sintering; and (ii) the development of a model of agglomerate sintering that removes the physically unrealistic constraints of the classical sintering model, notably the limitation to the very early stage of neck growth and to a single mechanism of material transport to the neck region.

3 Aerosol Aggregation Kinetics

3.1 Experimental Determination of the Collision Frequency Function

Although predictions of the growth of aerosol aggregates have been made using this and other collision aggregation models, no direct experimental measurements of the collision frequency function have been made. Hence, a major focus of this program is the experimental determination of the collision frequency function. The measurement of the collision frequency for aggregation is based upon mixing size–classified aggregate aerosols of two different particle mobility ranges. The particles are then allowed to aggregate at room temperature. The resulting aerosol is then analyzed to determine the extent of aggregation.

The key to this experiment is the size classification of the aggregate aerosol. A polydisperse aerosol is produced by hydrolysis of titanium tetraisopropoxide in the fume generator. Two DMAs are used to extract mobility classified fractions from that size distribution. The two aerosols are mixed together, and then allowed to coagulate at room temperature to minimize structural rearrangements of the aggregates as they coagulate. The size distribution of the mixed aerosol is measured before and after a long residence time in a coagulation flow tube reactor using a differential mobility classifier with a condensation nucleus counter as a detector. Initially, the same DMA/CNC combination was used to determine the size distribution before and after coagulation, employing carefully balanced plumbing between the sampling points at the opposite ends of the reactor to keep losses in the sampling lines from biasing the measurements. This system proved to be unstable, however. The experiment was modified to use only a single DMA for classifying the agglomerate particles while using the other two DMAs to measure the size distribution simultaneously at the inlet and at the outlet of the coagulation reactor, thereby limiting the experiments to the measurement of the collision frequency function for equali sized particles. This system was sufficiently stable to allow quantitative measurements to be made. The initial measurements, which allowed a residence time of 40s, are summarized in Fig. 1. The error bars in the plot show the estimated uncertainty in the measured collision frequency function. The measured collision frequency function is significantly greater than that predicted theoretically, although the large error bars make it uncertain whether the difference is due to error or is real. To overcome this, it will be necessary to allow a greater time for coagulation. Hence, a longer coagulation chamber was constructed.

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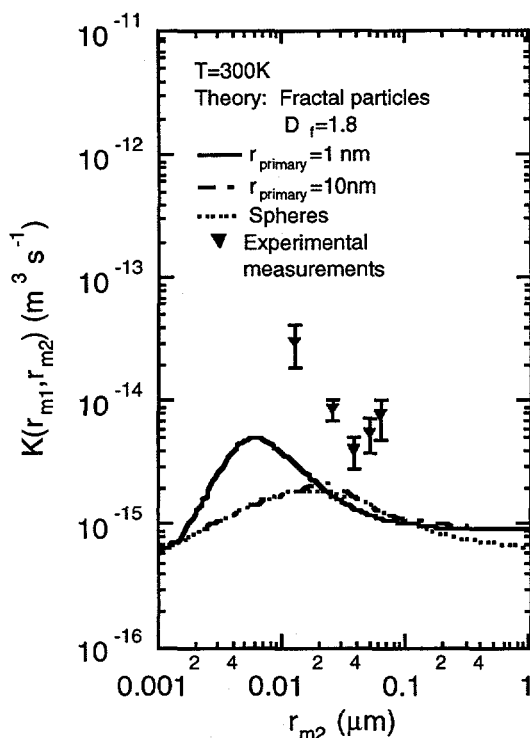
Figure 1: Measured collision frequency function for coagulation of equal size TiO_2 agglomerate particles.

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