Combustion Fume Structure and Dynamics

CONTRACT NUMBER: DE-FG22-90PC90286
CONTRACTOR: California Institute of Technology, Pasadena, CA 91125
PRINCIPAL INVESTIGATOR: Richard C. Flagan
PETC PROJECT MANAGER: Philip M. Goldberg
PERIOD OF PERFORMANCE: 2/16/94 –8/15/94

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.

This project comprises theoretical and experimental investigations of the dynamics of aggregate aerosols produced as pyrogenous fumes. For the pruposes of modeling the dynamics of these complex structures, the particles have been characterized and modeled as having fractal structure. 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. Experimental and theoretical investigations of the individual processes involved in the aerosol evolution, i.e., sintering and aggregation are studied independently using model systems. Theoretical investigations have paralleled the experimental studies to help to interpret the experimental results and as a step toward the develop of quantitative predictive models.

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

DISCLAIMER

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.

We have undertaken a theoretical investigation of the sintering of bisphere agglomerates, extending the classical descriptions while relaxing some of the key constraints in those models. Notably, we have developed a modified geometry, illustrated in Fig. 1, and numerical procedures that conserve mass throughout the sintering process, extending the predictions well beyond the early neck growth limit of classical description, i.e., beyond a ratio of the neck radius x to the initial sphere radius a_0 of $x/a_0 \sim 0.3$. Figure 2 compares the predictions of the present model with the classical theory. While the two descriptions are in excellent agreement below this limit, the time required for complete densification is significantly longer than predicted with the previous models.

The new sintering model also allows examination of the simultaneous contributions of multiple transport mechanisms to the structural rearrangements of agglomerate particles. Using this model, an extreme estimate of the influence of the thin (nanometer scale) oxide layer formed on the agglomerate particles was made by setting the surface diffusivity to zero. The predicted neck growth was then brought into agreement with the experimental observations when published transport properties were used for all other mechanisms. This result not only supports the validity of our model, it also indicates the sensitivity of the sintering process to the details of the environment in which the sintering occurs. Unless the chemical and physical environment is well characterized, a priori prediction of the structural rearrangements of agglomerate particles will frequently lead to erroneous results.

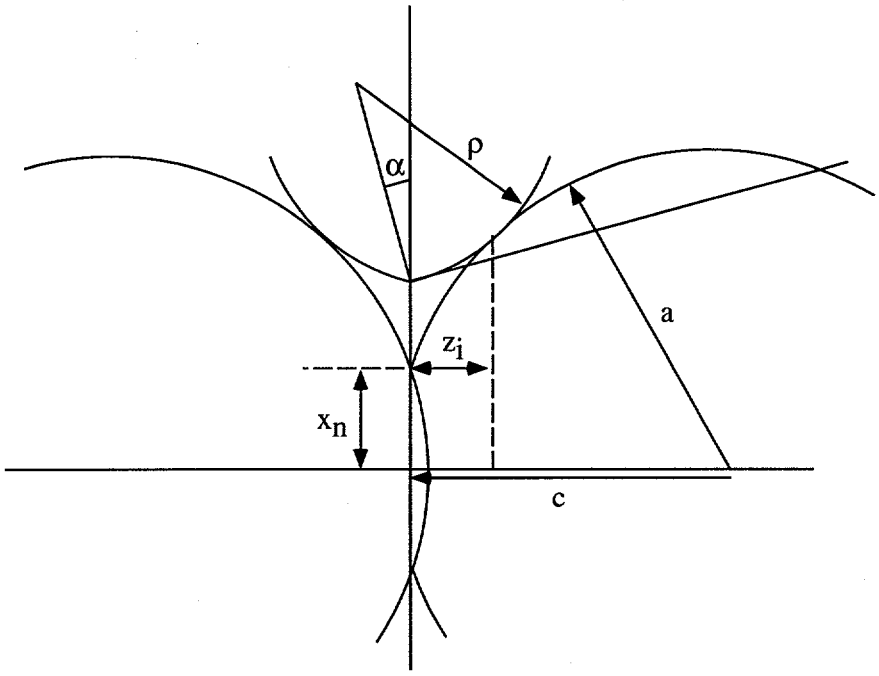

Figure 1: Model geometry used in the simulation of the sintering of bispheres.

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. Mobility classified agglomerate particles are allowed to coagulate, and the change in the size distribution is measured using separate differential mobility analyzers at the inlet and outlet of the coagulation reactor. Initial experiments showed substantial uncertainty due to the limited coagulation that occurred in a 40 s residence time. A longer (3m) reactor was constructed to allow the coagulation time to be increased to 344 s, greatly reducing the uncertainty in the experimental measurements, as illustrated in Fig. 3. Even with the reduced uncertainty, the predicted collision rate coefficient was significantly greater than the

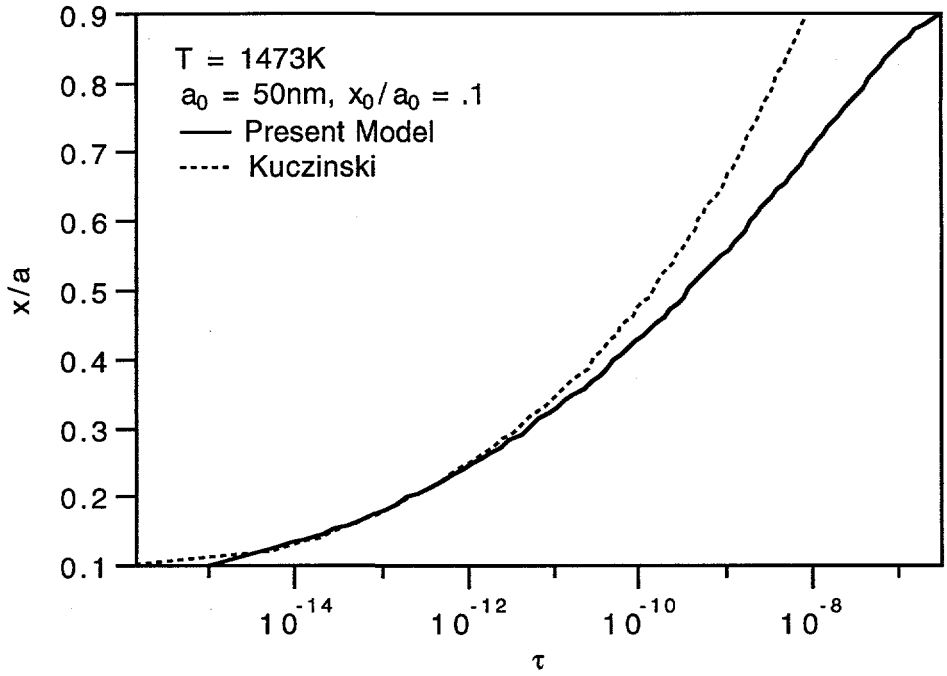

Figure 2: Simulation of the sintering of a silicon bispheres as calculated using the classical sintering theory with the predictions of the present model vial surface diffusion alone.

theoretical predictions. To verify that this difference is real, experiments were also conducted using dense NaCl particles, shown as open points. The latter data are in close agreement with theoretical predictions for particles larger than about 20nm radius. Below this size, Van der Waals forces are expeced to enhance the coagulation rate, so the deviation of the measurements for the smallest particles is not unexpected. The larger deviations between theory and measurement for agglomerate particles may result from interparticle forces or from an incorrect estimate of the collision cross section for the agglomerate particles.

References

[1] Flagan, R.C., and Friedlander, S.K. In *Recent Developments in Aerosol Science* (D.T. Shaw, ed.), pages 25–29. John Wiley & Sons, New York, (1978).

[2] M. Neville and A. F. Sarofim. The stratified composition of inorganic submicron particles produced during coal combustion. In *Nineteenth Symp. (Int.) on Combustion*, pages 1441–1449. The Combustion Institute, Pittsburgh, PA, 1982.

[3] R. J. Quann and A. F. Sarofim. Vaporization of refractory ioxides during pulverized coal combustion. In *Nineteenth Symp. (Int.) on Combustion*, pages 1429–1440. The Combustion Institute, Pittsburgh, PA, 1982.

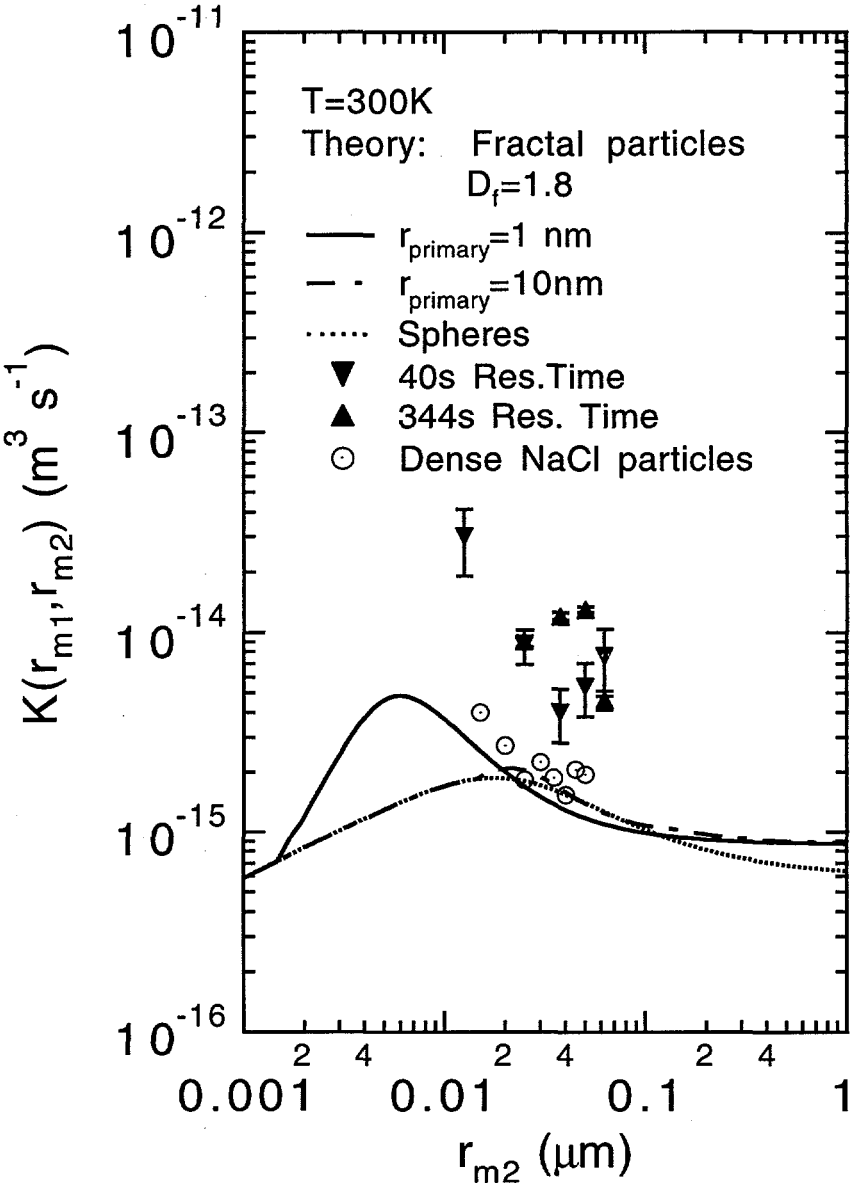

Figure 3: Comparison of measured collision frequency function for equal sized agglomerate and dense particles with theoretical predictions.