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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)

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.

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. Simplistic models have previously been developed that track the evolution of a few moments of the the particle size and structure distribution, i.e., number, surface area, and mass concentrations per unit volume of gas, or that track the number of primary particles that comprise the larger agglomerates. For these analyses, the flow of material as agglomerates densify is treated with variants of the Frenkel/Kuczinski sintering model. That model describes the early phase of neck formation, and is generally limited to the neck growth less to sizes less than about 30% of the primary particle size, i.e., $x/a < 0.3$. Models developed for different sintering mechanisms reveal differences in the size dependence of the sintering rate for the various mechanisms.

Uncertainties in the predictions are large due to incomplete knowledge of the relevant transport properties (surface diffusivity, self-diffusivity, viscosity, etc.). Qualitative agreement with experimental observations can be obtained if the transport properties are treated as fitting parameters, but a priori predictions frequently lead to orders of magnitude discrepancies in sintering rates.

An experimental investigation of the sintering rates of aggregate particles has been 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 are produced by high temperature consolidation of particles produced from volatile precursors. While still entrained in the carrier gas flow, the spherical particles are then allowed to aggregate at low temperatures to form doublets or bispheres. Finally, the bispheres are heat treated in a second flow reactor at controlled temperatures and residence times to induce sintering. Particles at various stages of densification are collected and analyzed using transmission electron microscopy.

We have previously reported on extensive experiments have conducted using bispheres of elemental silicon which sinters primarily by surface diffusion. The results from those experiments illustrate important features of aggregate coalescence. The experiments with bispheres are being used to validate aggregate sintering models that have been developed in this project.

Important physics of sintering of larger aggregate particles are excluded from the bisphere experiments, however. In the bispheres, each particle contacts only one other particle, whereas in typical combustion fume particles each primary particle is connected to two or more other primary particles. Preliminary experiments on the effect of sintering of aggregate particles on their structures were previously performed under this study by forming particles at different temperatures. The fractal dimension of the aggregate particles increased with synthesis temperature, but sintering, coagulation, and condensation all took place simultaneously. Although representative of the conditions of ash fume formation in coal combustion, the conditions of those experiments were too complex to allow detailed mechanistic models of aggregate sintering to be tested. Experiments have also been performed in which an aggregate aerosol produced under the conditions described above was diluted to suppress further coagulation and then processed at high temperature while still entrained in a nonreactive gas flow. Though a major improvement on the former experiments, the structures of the aggregate particles were too complex for detailed analysis.

To study the effect of sintering independent of other dynamic processes, studies of the sintering of model aggregates have been undertaken. The system used for these experiments is illustrated in Fig. 1. To take advantage of the understanding gained in the bisphere experiments and the existing particle generation apparatus, the initial experiments have been performed with aggregates elemental silicon. Primary particles are produced by reaction of a gaseous precursor, silane in the initial experiments and alkoxide in future experiments. The agglomerate particles thus produced were then heated to high enough temperatures to fully densify them. The primary particles thus produced were then allowed to aggregate at room temperature, forming the model aggregates for study. Note that, throughout the processes described above and the additional processing steps that follow, the particles are entrained in a carrier gas and are processed in the aerosol phase.

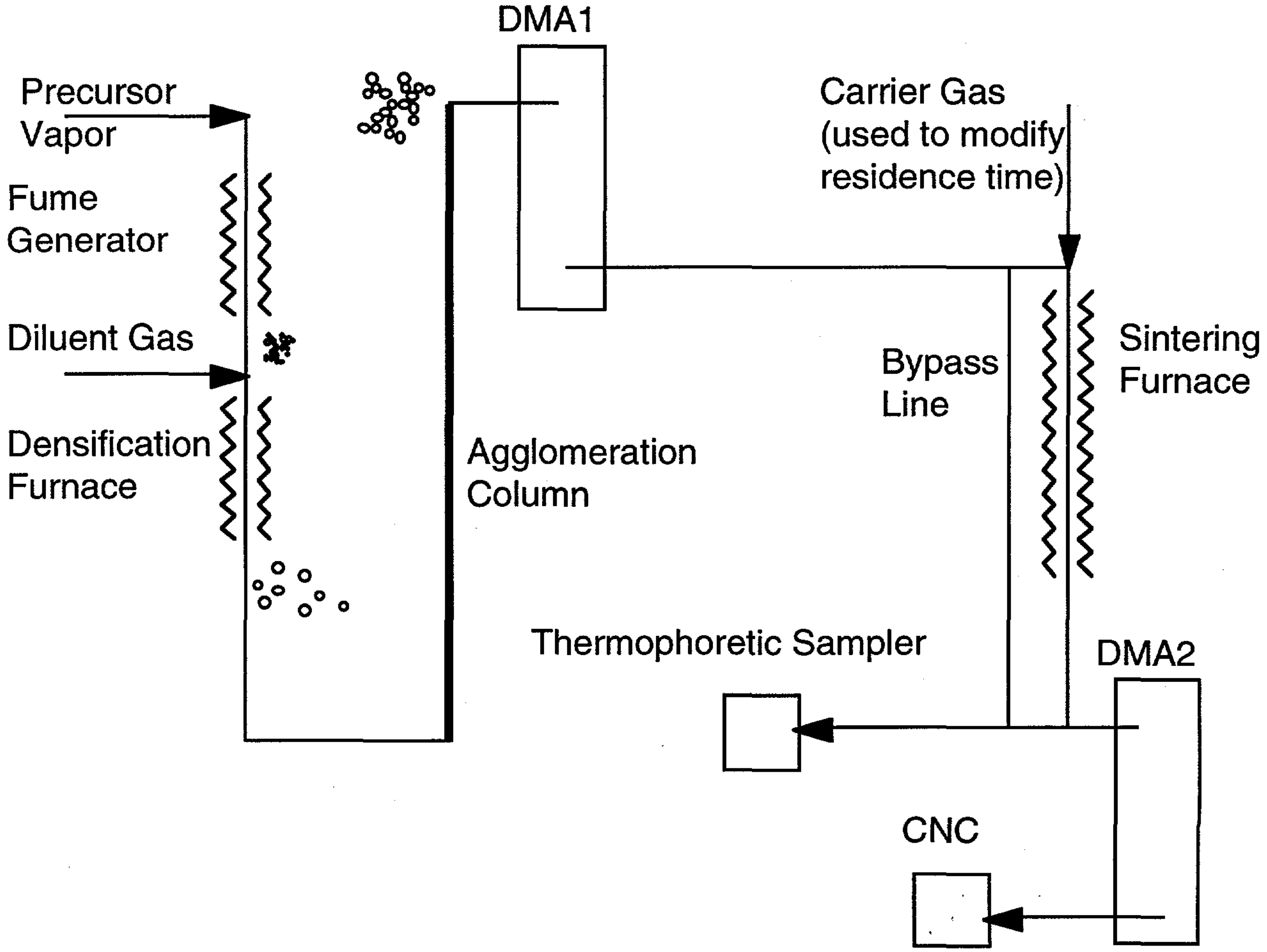

Figure 1: Schematic diagram of the experimental system used for aggregate particle sintering studies.

Densification experiments were performed using mobility classified aggregates. The aggregate particles were classified using a TSI differential mobility analyzer (DMA), which is illustrated in Fig. 2. Samples of the classified aggregate particles were collected on transmission electron microscope (TEM) grids for TEM analysis of the particle structure. The aggregate particles were heat treated for various residence times and temperatures by passing the classified aerosol through a third furnace. Samples of the heat treated particles were collected on TEM grids for study of the structural changes. The size distribution of the classified aerosol at varying degrees of heat treatment was measured using a second differential mobility analyzer with a TSI Model 3076 condensation nucleus counter as a detector.

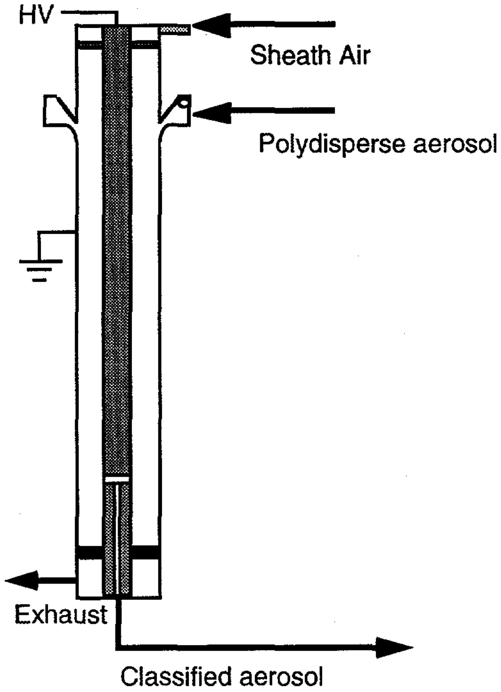

Figure 2: Schematic diagram of the differential mobility analyzer.

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.

Although the problems encountered in this experiment are specific to the material chosen for the first model aerosol, the importance of the surface condition of the particles is clearly illustrated. Future experiments will address the surface state of the aerosol studied to probe this effect.

Aggregate sintering experiments using model silicon aggregates are now underway. The silicon experiments will be followed with similar measurements of the sintering of metal oxide particles produced by pyrolysis of suitable metal alkoxides or other volatile precursors.

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. The overall experimental system is illustrated in Fig. 3. A polydisperse aerosol will be produced by

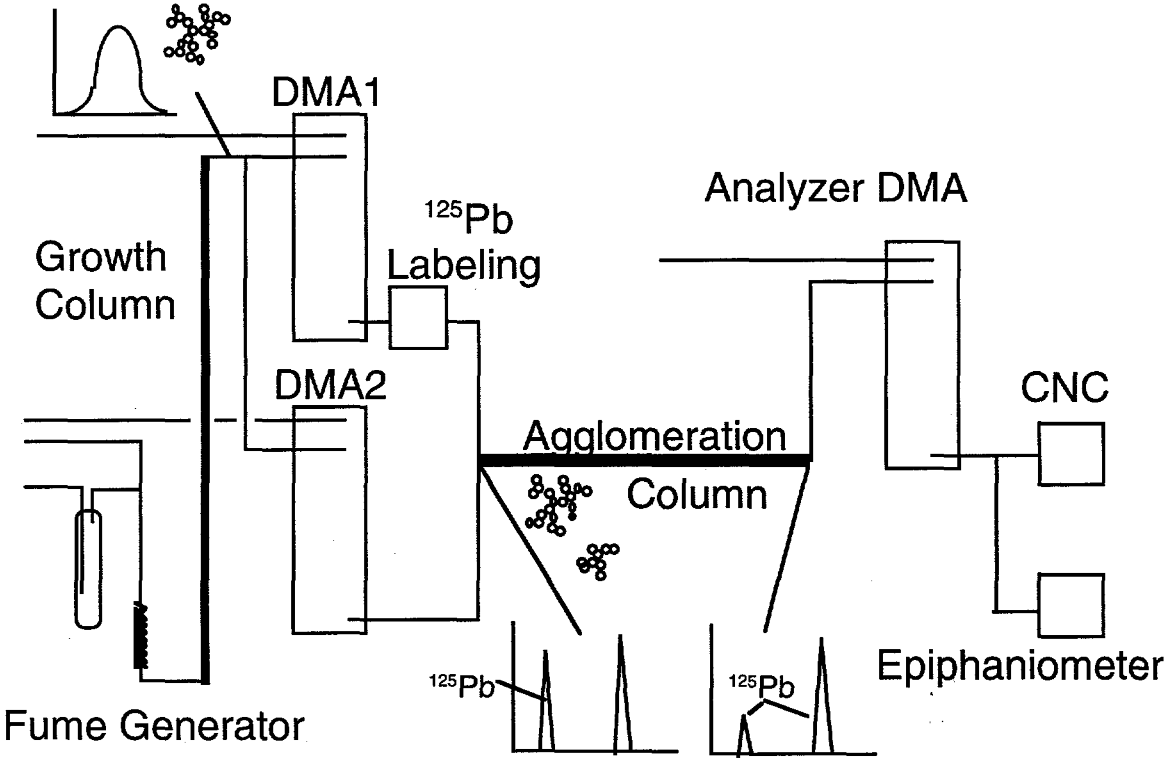

Figure 3: Apparatus used for direct measurement of aggregation rates.

hydrolysis of titanium tetraisopropoxide in the fume generator. Two DMAs are used to extract mobility classified fractions from that size distribution. This is illustrated in Fig. 4 which shows the particle size distributions for the original source aerosol and for two mobility classified fractions. The number concentrations in the classified aerosol are lower than that of the original fume due to the low efficiency charging that is necessary to minimize the numbers of particles carrying multiple charges. Even so, each of the mobility fractions shows several peaks due to the presence of multiply charged particles. Three peaks appear in the distribution due to multiple charging. The peak at smaller size than the main peak consists of particles that passed through the first DMA with a single charge and acquired two charges in the second DMA. The peak to the right of the main peak in each fraction arises from particles that were doubly charged in the first DMA and, therefore, appeared to be smaller than their true size. The complications introduced into the data analysis are minor due to the large difference in the heights of the peaks.

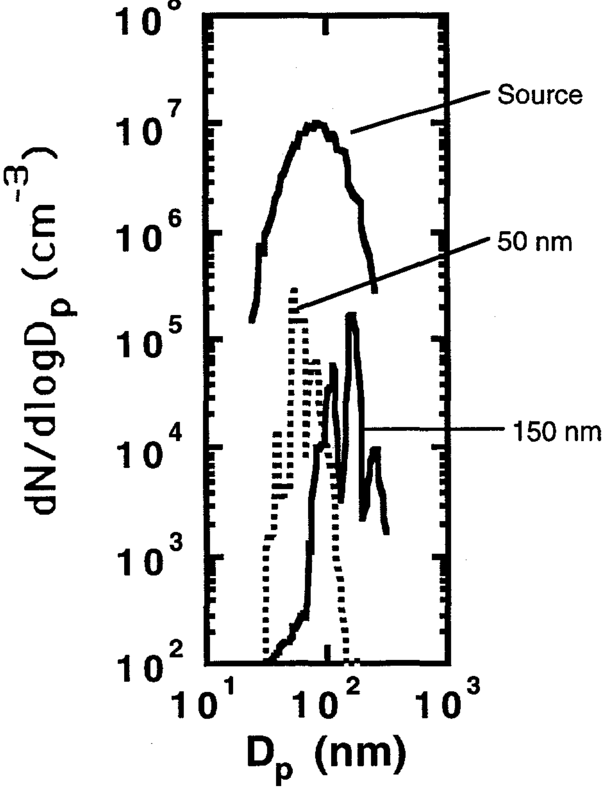

Figure 4: Particle size distributions for source aerosol produced by the fume generator and two mobility classified fractions.

The initial plan for this experiment was to label the smaller of the size fractions with ^{210}Pb using an Epiphaniometer that has been obtained on loan from the Paul Scherrer Institute in Zurich Switzerland. In the epiphaniometer, the labeled aerosol is collected on a filter. Radioactive decay from the labeled particles provides a sensitive measure of the transfer of material to the target particles. Because the radioactive label makes the added mass distinguishable from the original particle mass and can be detected at very low levels, the epiphaniometer should allow coagulation to be measured with negligible change in the particle size distribution. All that is required is to use a classifier to separate the larger, initially unlabeled particles from the smaller ones that are initially labeled.

The epiphaniometer was originally developed for the measurement of the surface area of the atmospheric aerosol in remote, and therefore, relatively clean locations. The instrument is fully automated and optimized for those conditions. Unfortunately, this optimization imparts the instruments with a sensitivity to pressure variations that has proven to be difficult to reconcile with the conditions of our experiment. Although the instrument could be modified to facilitate the planned measurements, the terms of agreement in borrowing the instrument preclude such modifications.

Because of these difficulties in using the epiphaniometer, we have turned our attention to the measurement of aggregation directly from the evolution of the size distribution. While the epiphaniometer measurements would monitor the aggregation by probing mass addition to the larger aggregate particles, the size distribution change that would result from a single fine particle addition is generally too small to detect. Instead, the loss of the fine particles must be measured with high precision. The resolution of the DMA is sufficient for these measurements, but longer coagulation times will be required to obtain large enough reductions in the fine particle concentrations.

During this reporting period, limited measurements have been made on the self–coagulation of particles in one mobility fraction. Although the experiment is relatively simple since it requires only two DMAs, this represents the most severe case since the collision frequency function for this case is much lower than that for particles of different sizes. Figure 5, which shows the shift in the size distribution that results from self-coagulation of an aerosol of 55 nm TiO_2 aggregate particles, clearly demonstrates the ability to measure the shift in the size distribution due to coagulation. Future experiments will focus on the measurements of coagulation of dissimilar sizes of particles and on the characterization of the structures of those 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.

[4] Kauppinen, E. I. Aerosol Formation in Coal Combustion Processes. *J. Aerosol Sci.*, **22**:S451–S454, (1991).

[5] Fuchs, N.A. *The Mechanics of Aerosols.* Pergamon Press, New York, NY, (1964).

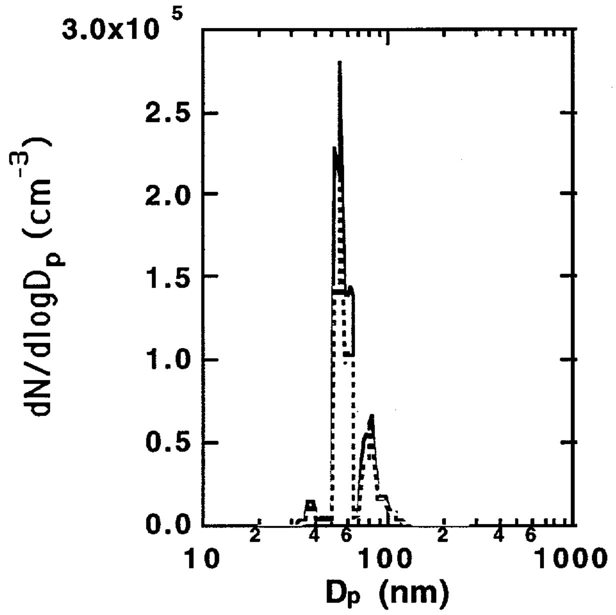

Figure 5: Size distribution change resulting from coagulation of an aggregate aerosol of 55 nm mobility classified TiO_2 particles.

[6] Friedlander, S.K. *Smoke, Dust, and Haze*, page 195. Wiley-Interscience, New York, NY, (1977).

[7] Seinfeld, J.H. *Atmospheric Chemistry and Physics of Air Pollution.* John Wiley, New York, NY, (1986).

[8] S. R. Forrest and T. A. Witten. *J. Phys. A.: Math. Gen.*, 12:L109–L117, 1979.

[9] Meakin, P. In *On Growth and Form*, pages 111–135. Martinus Nijhoff Boston, (1986). (H. Stanley and N. Ostrowsky, eds.).

4 Papers and Presentations during Reporting Period

1. R. F. Flagan, "Dynamics of Pyrogenous Fumes", Presented at the International Workshop on Trace Element Transformations in Coal-Fired Power Systems, Scottsdale, Arizona, April 19 – 22, 1993. *Fuel Processing Technology, in press.*

2. R. C. Flagan, "Measurements of the Size Distribution and Structure of Ultrafine Aerosol Particles," presented at Fluid–Particle Interactions III, Engineering Foundation Conference, Davos, Switzerland, May 9-14, 1993

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