Particle Formation and Growth in Power Plant Plumes

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NOTICE

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EPRI PERSPECTIVE

PROJECT DESCRIPTION

Sulfur oxides and nitrogen oxides have been implicated as major contributors to visibility impairment and acidic precipitation in the United States. Formation of small particles that scatter light, producing "haze" and act as condensation nuclei for raindrops has been reported to occur in the plumes of fossil-fueled power plants as well as other locations. The studies described in this two-volume report involved theoretical and field investigations of the rates of formation and size distributions of particles in six coal-fired power plants in the midwestern and western United States.

PROJECT OBJECTIVES

The objectives of the project, which spanned some five years, were to measure particle size distributions in coal-fired power plant plumes at various locations and under a variety of meteorological conditions. In addition, a three-dimensional numerical model was developed and refined for simulating particle formation and growth in plumes.

PROJECT RESULTS

The measured rates of conversion of sulfur dioxide to particulate sulfate ranged from 0 to 5.7% per hour. However, most observations fell within a narrower range of 0.1 to 1.0% per hour. Reaction rates were all found to depend on travel time from the stack and ultraviolet light intensity. The PHOENIX model predictions of maximum gas-to-particle conversion rates that occur near the edges of the plume are in agreement with the measurements. Elsewhere in the plume, the model predictions were about a factor of 10 lower than the measurements. The PHOENIX model has been applied in recent years by other sponsors to the specific question of haze generation in western plumes.

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SUMMARY

RESULTS OF THIS STUDY

Gas-to-particle (g-to-p) conversion rates have been measured in the plumes of six coal-fired power plants situated in the West and Midwest of the United States. The conversion rate was estimated from measurements of the changes in the total volume of particles in the plume, the production rate of Aitken nuclei, and three different particulate filter analysis techniques (flash vaporization, X-ray fluorescence and ion-exchange chromatography). Comparison of sulfate concentrations derived from X-ray fluorescence and ion-exchange chromatography showed fair agreement--indicating that most of the particulate sulfur is sulfate. Comparison of g-to-p conversion rates estimated from the changes in total particle volume with those derived from particulate filter data showed, in general, that the major portion of the g-to-p conversion product was sulfate. However, in some instances, the g-to-p conversion rate based on total particle volume was higher than the rate based on particulate filter analysis; this suggests that conversion products other than sulfate may sometimes be formed in power plant plumes.

One possible conversion product, other than sulfate, which has been postulated to be produced in power plant plumes, is nitrate. To evaluate this hypothesis some nitrate measurements were made in the plumes. The data suggest that nitrate formation, in general, was of little importance during the flights in which measurements were obtained. An estimate of the NO_x-to-nitrate conversion rate was made for one of the cases studied at the Big Brown (Texas) power plant and was found to be $\sim$0.4%/hr for distances of 4.8 to 43.2 km. The SO_2-to-sulfate conversion rates, measured simultaneously, ranged from 0.7 to 2.8%/hr and increased with travel time from the stack.

The rates at which new particles were nucleated in the plumes were evaluated and the ratio of this nucleation rate to the rate of formation of new particle volume was calculated. The ratio was found to range from 2.7×10^2 to 3.9×10^5 particles μm^{-3} with a mean value of $7.4 \times 10^4 \pm 1.2 \times 10^5$ particles μm^{-3}. This ratio is

indicative of the fraction of g-to-p conversion product which forms new particles --the remainder of the conversion product condensing directly onto already existing particles. The large variation in this ratio, some of which is attributable to differing plant locale, suggests regional differences in the g-to-p conversion process. Results from the PHOENIX plume model suggest that it should be possible to predict this ratio on the basis of a modified version of the theory of McMurry (27). The PHOENIX model outputs suggest the importance of the above ratio in determining the light-scattering coefficient and visibility degradation.

Further analysis was made of the relationship between the rates of formation of new particle surface area and new particle volume. The data were found to be in fair agreement with the theoretical relationship of McMurry and Friedlander (64) in which the particle surface area varies as the rate of formation of new particle volume raised to the $3/5^{th}$ power. This suggests that the size distribution of the particles in the plume becomes self-preserving.

The SO_2-to-particulate sulfate conversion rates were found to range from 0 to 5.7%/hr--the higher rates generally occurring in the Southwest. This range is in agreement with previous studies conducted both in the Eastern United States and at the Four Corners power plant in New Mexico. The SO_2 g-to-p conversion rate was also found to depend on travel time from the stack and UV light intensity.

Both the physics and the chemistry of the g-to-p conversion process(es) suggest that the dominant (though not necessarily the sole) conversion mechanism in the plumes studied is the oxidation of SO_2 by OH radicals. A significant correlation ($r = 0.9$) was found between the conversion rates and a parameter indicative of this reaction.

The results of this study have suggested several areas in which further efforts might yield valuable information.

While the data collected in this study suggest that the SO_2-to-sulfate conversion process is predominantly SO_2 oxidation by OH radicals, this has not been conclusively demonstrated. An extension of the present work would be to correlate measured g-to-p conversion rates with actual measurements of OH concentrations. Furthermore, this study was conducted preferentially in fair weather when free

radical reactions would be at their maximum importance. More data should be gathered under cloudy weather conditions when aqueous processes might dominate.

The question of the source of the variation in the fraction of new particle volume that appears as new particles has not been fully answered by this study. More precise data on particle surface area, volume formation rates, collision frequencies, and particle nucleation rates are necessary to determine possible relationships between these parameters and the fraction of new particle volume that forms new particles. The use of a refined version of the theory of McMurry (27) in the PHOENIX plume model appears to be a potentially useful tool in attacking this question.

Further data are needed on nitrate concentrations in power plant plumes in order to evaluate more fully the importance of nitrate formation to the overall g-to-p conversion process. In view of the low nitrate concentrations that we measured, much larger sample volumes will be needed than those obtained in this study; volumes as high as 2000 liters may be necessary. Analysis for particulate organics should also be carried out together with a more detailed analysis of background hydrocarbons to identify possible particulate organic precursors.

The results of this study suggest that regional differences may exist in the g-to-p conversion process. Sufficient data should be gathered at each of several different locales to allow parameters such as the ratio of particle nucleation rate to particle volume formation rate to be determined with great statistical precision at each site. Statistically meaningful intersite comparisons could then be made.