



## Project Summary

# Fundamental Study of Sulfate Aerosol Formation, Condensation, and Growth

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**A theoretical and experimental program was performed to study the formation and growth of sulfate particles. Existing theoretical models on acid particle formation and growth were reviewed and evaluated. The formation and growth of sulfate particles during slow cooling, rapid cooling, and dilution cooling of flue gas were experimentally determined and compared with theories.**

**The experimental results show that the temperature at which the self-nucleation of sulfuric acid occurs is lower than the acid dew point temperature. Thus, if the flue gas is slowly cooled to between dew point and nucleation temperature, it is possible to force the sulfuric acid to condense out on surfaces, rather than forming fine particles.**

**The theories, experimental methods, and results are described in this report.**

***This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

### Introduction

Primary sulfates are significant pollutants, contributing to the formation of acid rain, reduced atmospheric visibility, and human respirable diseases. To illustrate the magnitude of the sulfate problem, more than one-third of the airborne respirable particles in the Eastern U.S. are in the form of sulfate.

A major source of atmospheric sulfate particles is the chemical reaction of  $\text{SO}_2$  and particles in the ambient air. However, control of secondary sulfates through direct control of  $\text{SO}_2$  emissions has not generally resulted in a decrease in atmospheric sulfate. Therefore, it is worthwhile to consider control techniques for primary sulfates.

Existing particle control systems do not effectively remove condensable aerosols because the aerosol precursors are often in the vapor state when they pass through the control device. Although the vapors usually will condense in a wet scrubber, they often form ultrafine particles which are very difficult to capture.

The first step toward developing acceptable technology for reducing condensable aerosol emissions is to obtain an adequate data base and understand the mechanisms involved: the condensation, formation, and growth of sulfate aerosols in a simulated flue gas environment.

Under contract to the U.S. Environmental Protection Agency, A.P.T., Inc., performed a detailed theoretical and experimental study of sulfate particle formation and growth. The theories, experimental methods, and results are described in this report.

### Objectives

This research was a theoretical and experimental study of sulfate aerosol formation and growth under conditions that exist in industrial smoke stacks and the near-stack plume. The objectives were to develop the fundamental data and mathematical models necessary to design emission control strategies and control devices for sulfate condensation aerosols.

## Approach

The general approach was first to define the mechanisms by which  $\text{SO}_2$  and  $\text{SO}_3$  are converted to sulfate particles and then use this knowledge to develop optimum control.  $\text{SO}_2$  and  $\text{SO}_3$  can convert to sulfate particles by:

1. Condensation of sulfuric acid vapor (or water-vapor-associated  $\text{SO}_3$ ) to form sulfuric acid drops.
2. Condensation of sulfuric acid vapor on pre-existing particles such as fly ash, liquid drops, and acid drops.
3. Sorption of  $\text{SO}_2$  by liquid or solid particles, followed by oxidation of  $\text{SO}_2$  to sulfate.
4. Gas-phase oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  which is subsequently condensed by mechanisms 1 and 2.
5. Chemical reaction of acid vapor with solid or liquid particles.

This study emphasizes sulfate formation by mechanisms 1 and 2. Mechanism 4 is not likely to happen in industrial smoke stacks, and mechanisms 3 and 5 are system dependent and difficult to generalize.

Sulfate formation due to condensation is a physical process in which the gas temperature must be below the acid dew point. Gas can be cooled by heat transfer to the surroundings, quenching (such as by introducing water sprays), and mixing with cold gas. All three cooling processes could occur in industrial smoke stacks and in near-stack plumes. Therefore, sulfate formation in typical flue gas mixtures during slow cooling, rapid quenching, and dilution cooling was experimentally studied. The results obtained in this study plus published data were then used to verify sulfate formation models and develop emission control technologies.

## Experiments

### Apparatus

Figure 1 shows the experimental system design, which was basically the same for all experiments. It consisted of a flue gas simulator for supplying acid-laden gas for various cooling apparatus arrangements. Major components of the flue gas simulator included an acid vapor generator, a steam generator, a fly ash particle generator, and a  $\text{SO}_2$  gas cylinder.

Sulfuric acid and water vapors were generated by evaporating dilute sulfuric acid and water at controlled rates. Fly ash particles were produced by re-dispersion.  $\text{SO}_2$  was metered into the flue gas simulator from the gas cylinder. Room air was used as the carrier gas because the amount of oxygen and the presence of  $\text{CO}_2$  and nitrogen oxides in the flue gas have no effect on sulfate particle formation in the stack.

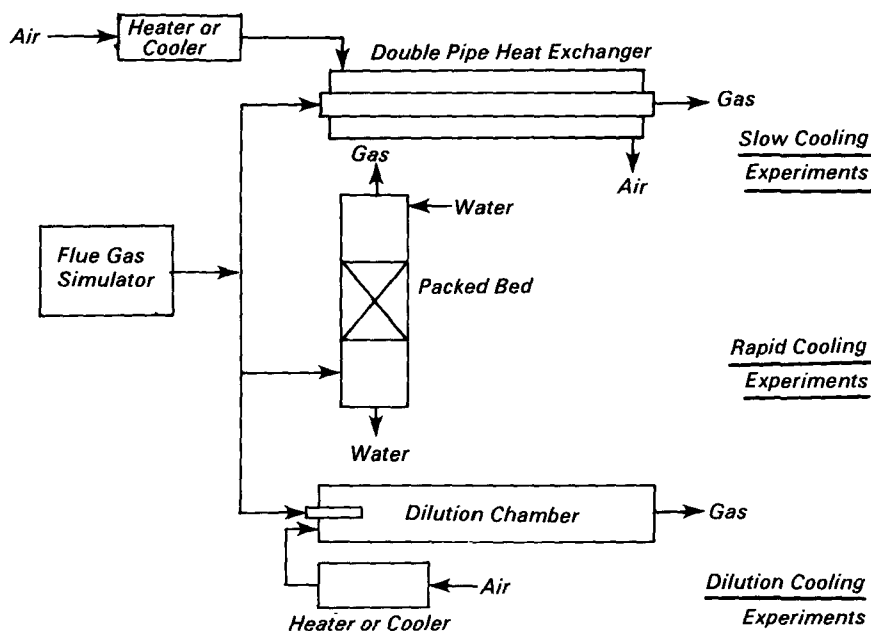


Figure 1. Experimental system design.

The following cooling apparatus was used in the experiments:

1. Slow cooling — double-pipe heat exchanger.
2. Rapid quenching — packed-bed column.
3. Dilution cooling — parallel-stream dilution chamber.

### Measurement Methods

Gas samples at the cooling apparatus inlet and outlet were obtained simultaneously to determine:

1. Inlet acid vapor, water vapor,  $\text{SO}_2$ , and fly ash particle concentration.
2. The amount of acid vapor condensed on existing particles.
3. Concentration of newly formed acid particles.
4. The amount of acid vapor condensed on walls.
5. Particle size distribution.

Figure 2 shows the sulfate sampling system. Train "A" (used at the inlet) consisted of a cascade impactor (or quartz filter) followed by a condensation coil, a quartz filter, three impingers, and gas metering and moving instruments. Train "B" (used at the outlet) consisted of an impactor (with final filter removed) connected in series with a screen diffusion battery, a quartz filter, a condensation coil, another quartz filter, three impingers, and gas metering and moving instruments. The instruments upstream of the condensation coil were heated to and maintained at gas temperature. The water-cooled

condensation coil was maintained at between 60 and 90°C when  $\text{SO}_2$  was injected.

The acid collected by the impactor, diffusion battery, and filter was analyzed by extraction and titration. Acid collected by the condensation coil and impinger was determined by washing followed by titration.

## Results

### Rapid Quenching

Rapid quenching experiments simulated the formation of sulfate particles in a scrubber. The quencher used in this study was a randomly packed bed of Berl saddles. The effects of acid vapor concentration (10 to 100 ppmV), water vapor concentration (5 to 15% by volume),  $\text{SO}_2$  concentration (0 to 1.3 g/m<sup>3</sup>), and quench water temperature (20 to 60°C) on nucleated acid particle size distribution were determined experimentally. The results are:

1. Higher water temperature and lower acid and water vapor concentrations resulted in higher concentration of fine acid particles. Low water temperature decreased the gas temperature and caused additional water vapor condensation on the nucleated particles. Decreasing the acid and water vapor concentration reduced the particle growth.
2. The presence of  $\text{SO}_2$  had no effect on acid-bearing particle nucleation.
3. In the presence of fly ash particles, acid-bearing particles were larger

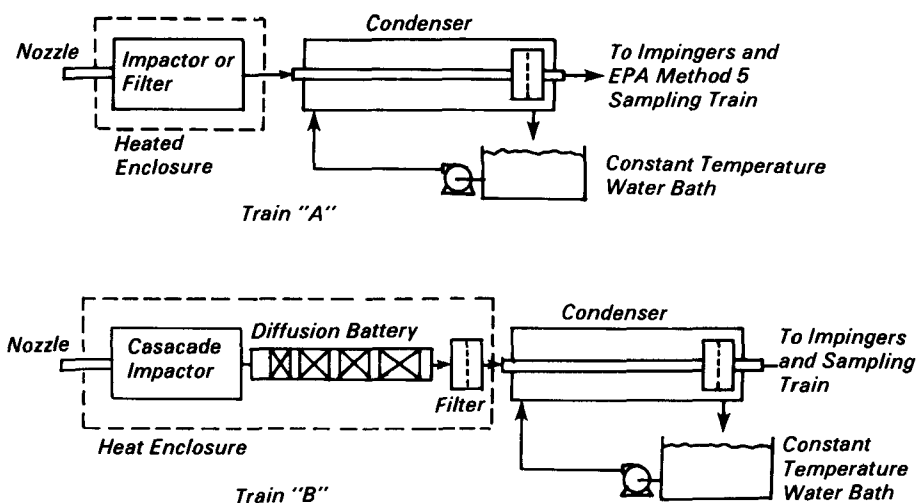


Figure 2. Acid concentration and particle size distribution sampling system.

because of condensation of acid vapor on the particles. Rapid quenching caused local high supersaturation of acid vapor; therefore, many very small acid particles were nucleated.

4. Downstream from the quencher, particle growth due to agglomeration was negligible.

### Dilution Cooling

Dilution cooling experiments simulated the formation of sulfate particles in the near-stack plume. The cooler was a concentric parallel-stream dilution chamber with dilution air forming a sheath around the flue gas. The effects of dilution air temperature, water and acid vapor concentrations, and the presence of SO<sub>2</sub> and fly ash particles on acid nucleation were studied. The results are:

1. The concentration of fine acid particles decreased with increasing dilution air temperature, decreasing acid vapor concentration, and increasing water vapor concentration.
2. SO<sub>2</sub> had no effect on acid particle nucleation.
3. The concentration of fine acid particles decreased in the presence of fly ash particles.

### Slow Cooling

Slow cooling experiments were relevant to the acid particle nucleation which could occur in industrial smoke stacks, dry pollution control devices such as electrostatic precipitators, and baghouses. The experiments were performed on a co-current, double-pipe heat exchanger with flue gas flowing in the center pipe. Acid particle

samples were taken where nucleation was observed to start. The experimental findings are:

1. Over 80% of the acid vapor was condensed on preexisting fly ash particles.
2. Higher acid vapor and lower water vapor concentrations led to the formation of many ultrafine acid particles.
3. SO<sub>2</sub> had no effect on acid particle nucleation.
4. Much acid vapor was condensed on walls upstream of the nucleation starting point.

## Comparison Between Theory and Experiments

### Nucleation Temperature

The nucleation of sulfuric acid particles involves two condensible species, water and sulfuric acid. For a given water and acid vapor concentration combination, the temperature at which nucleation of sulfuric acid particles starts can be predicted from thermodynamics and classical kinetic theory. In this study, the simplified equation used to predict the nucleation temperature was defined as the temperature which gives a nucleation rate of 1/cm<sup>3</sup>-s.

The calculations indicate that nucleation, once started, goes to completion quickly. Acid vapor is depleted in a very short time. The predicted nucleation temperature increases with increasing water vapor and acid vapor concentrations as shown in Figure 3. This means that less cooling of flue gas is needed to initiate the formation of acid particles if the acid vapor and water vapor concentrations are high.

Table 1 shows the predicted and measured nucleation temperatures. The measured acid particle nucleation temperatures varied around the predictions. Considering the uncertainties in vapor pressure and surface tension data, the agreement between theory and experiment is considered to be good.

### Slow Cooling

A mathematical model was developed to characterize the nucleation, condensation, and growth of sulfuric acid particles in a flow system. The model accounts for gas cooling, vapor loss to the wall, homogeneous binary nucleation, heterogeneous condensation on existing particles, diffusional loss of nucleated particles, and coagulation. A computer program, written to apply the model to slow cooling experiments: (1) uses a quasi-steady state approach, (2) follows a small element of fluid through the pipe, and (3) computes changes in temperature, vapor concentration, and particle concentration due to the above mentioned mechanisms in successive increments of distance along the pipe.

The measured gas cooling rate and wall condensation of acid vapor were compared to those predicted from heat and mass transfer. Because of entrance effects, the measured cooling rate and wall condensation of acid vapor were much higher than calculated.

### Capture Strategy Implications

The flue gas dew point temperature has been measured and predicted by numerous investigators. Although there are differences in dew point temperature given by different investigators, they are all much higher than the acid particle self nucleation temperature found in this study and predicted from classical nucleation theory (Figure 4). Thus, if the flue gas is slowly cooled to between dew point and nucleation temperatures, it is possible to force the sulfuric acid to condense out on surfaces, such as on fly ash particles and walls, rather than form fine particles. The experimental results obtained in this study show that this control method is feasible.

Avoiding rapid cooling of the flue gas minimizes acid particle nucleation. When flue gas much be quenched, the quench water should be as cold as possible. It would also help if additional water vapor, such as waste steam, is introduced into the gas stream (as in F/C, flux-force/condensation).

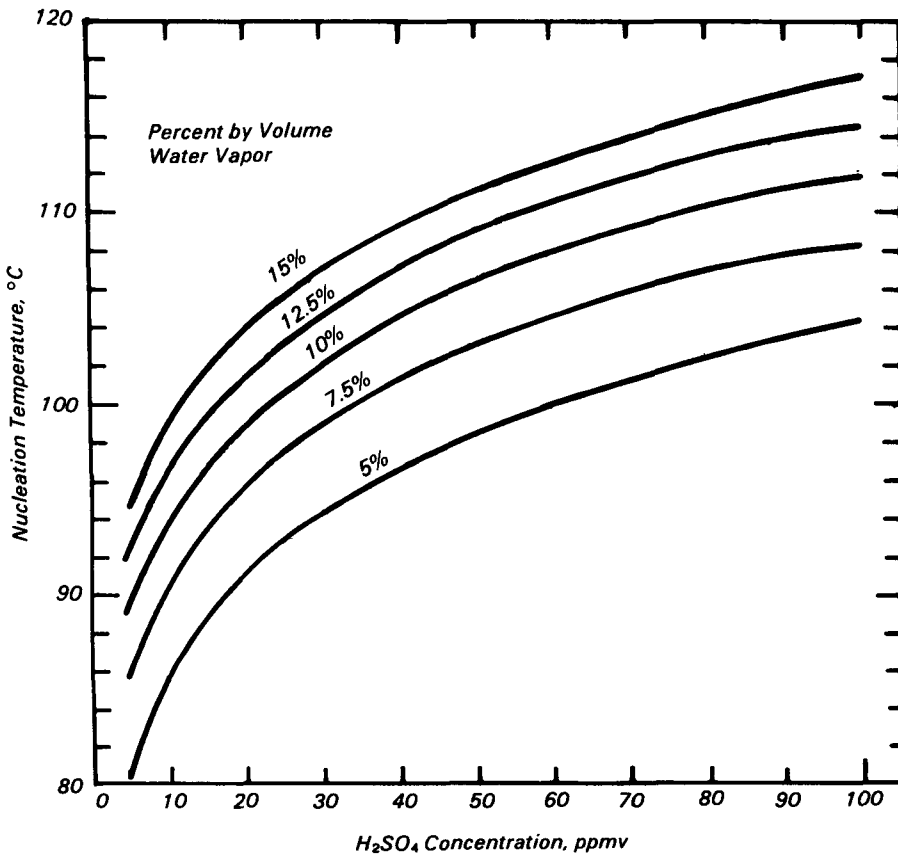
### Conclusions

Conclusions from this study are:

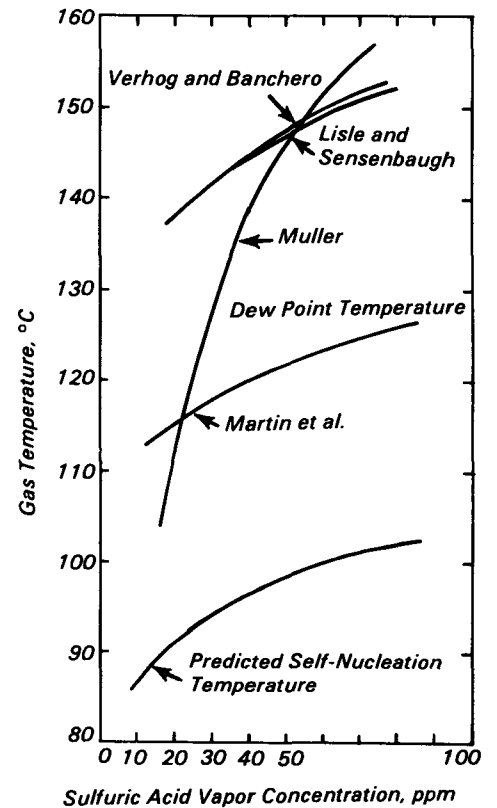
1. The temperatures at which the self-nucleation of sulfuric acid particles starts can be predicted from theory,

**Table 1. Predicted and Measured Nucleation Temperatures**

Run No.	Inlet		At Nucleation Point		Gas Temperature °C	Predicted Nucleation Temperature °C
	Acid Vapor Conc., ppm	Water Vapor Conc., Vol. %	Acid Vapor Conc., ppm	Water Vapor Conc., Vol. %		
116/01	83.4	10	65.2	10	106	105
116/02	49.9	5.5	39.6	2.8	96	97
116/04	52.1	4.7	46	2.9	99	98
116/05	61.9	14.5	60.4	14.5	109	113
117/01	29.0	10.1	11.6	4.9	104	95
117/02	40.2	5.0	19.9	2.5	86	91
117/03	35.5	13.8	26.1	12.2	103	105
118/01	22.1	10.1	19.3	9.6	96	98
118/02	27.6	14.0	17.3	11.6	103	102
119/01	22.0	10.1	4.6	10.6	91	99
119/02	31.4	4.8	17.7	3.1	101	90



**Figure 3. Predicted nucleation temperature.**



**Figure 4. Dew point and acid nucleation temperatures.**

and they agree with our experimental results. Thus, the sulfuric acid nucleation temperature for flue gas can be predicted, if the gas pressure, water vapor concentration, and SO<sub>3</sub> concentration are known.

2. Avoiding rapid cooling of flue gas minimizes the formation of fine acid particles.
3. While the presence of SO<sub>2</sub> has no effect on acid nucleation, fly ash particles

have great effect. Most of the acid vapor condenses on ash particles if the gas is cooled slowly.

4. Increasing the water vapor concentration in the gas stream increases the acid particle diameter by additional condensation or solution-induced particle growth.

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*Leslie E. Sparks is the EPA Project Officer (see below).*

*The complete report, entitled "Fundamental Study of Sulfate Aerosol Formation, Condensation, and Growth," (Order No. PB 84-179 886; Cost: \$17.50, subject to change) will be available only from:*

*National Technical Information Service*

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*The EPA Project Officer can be contacted at:*

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