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# OPACITY OF MONODISPERSE SULFURIC ACID AEROSOLS

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**Abstract**—The plume opacity and droplet diameters of a monodisperse sulfuric acid aerosol were calculated as a function of the initial $H_2SO_4$ concentration, initial $H_2O$ concentration and final gas temperature after cooling from an original stack gas temperature of 300°C. Calculation assumptions include heterogeneous heteromolecular condensation of $H_2SO_4$ and $H_2O$ onto monodisperse nuclei of 0.05 $\mu$m dia., three aerosol particle nuclei concentrations of $10^6$, $10^7$ and $10^8$ cm$^{-3}$ (at 300°C and 760 mm Hg); and a stack or plume diameter of 6 m. The calculated results show that for the conditions considered and with the stack temperatures in excess of 125°C, initial $H_2SO_4$ stack gas concentrations of 10 ppm or less will result in calculated opacities of less than 20% for a plume diameter of 6 m. The results show that the calculated opacity is significantly affected by the initial $H_2SO_4$ and initial $H_2O$ concentrations and the final gas temperature. The increases in the calculated opacities upon cooling of the stack gases are similar in general to the increases in the measured opacities between instack and outstack reported by Nader and Conner (1978) for an oil-fired boiler.

## NOMENCLATURE

| | |
|---|---|
| $B_E$ | light extinction coefficient (m$^{-1}$) |
| $C_i$ | concentration at initial conditions (ppm) |
| $C_f$ | concentration at final conditions (ppm) |
| $d$ | nuclei particle diameter (cm) |
| $D$ | acid droplet diameter (cm) |
| $g$ | gas |
| $\Delta G^*$ | free energy of formation of embryo nucleus droplet |
| $I$ | intensity of transmitted light |
| $I_0$ | intensity of incident light |
| $I/I_0$ | light transmittance (fractional) |
| $J$ | droplet nucleation rate (droplets cm$^{-3}$ s$^{-1}$) |
| $k$ | Boltzmann Constant ($1.38 \times 10^{-16}$ erg K$^{-1}$) |
| $K$ | specific particulate volume/light extinction coefficient (cm$^3$ m$^{-2}$) |
| $K_0$ | coagulation constant (cm$^3$ s$^{-1}$) |
| $L$ | illumination path length through plume (m) |
| $m$ | refractive index of particle relative to air |
| $m_{H_2O}$ | concentration of liquid water (g $H_2O$ m$^{-3}$ gas) |
| $m_{H_2SO_4}$ | concentration of liquid $H_2SO_4$ (g $H_2SO_4$ m$^{-3}$ gas) |
| $m_{acid}$ | concentration of liquid dilute sulfuric acid (grams m$^{-3}$) |
| $M_a$ | molecular weight of liquid dilute sulfuric acid |
| $M_{H_2O}$ | molecular weight of $H_2O$ |
| $M_{H_2SO_4}$ | molecular weight of $H_2SO_4$ |
| $N$ | total particle number concentration (particles m$^{-3}$) |
| $N_{av}$ | Avogadro's constant |
| $n_a$ | concentration of gaseous $H_2SO_4$ (molecules m$^{-3}$) |
| $n_0$ | nuclei concentration at time zero |
| $n(r)$ | particle number frequency distribution |
| $n_w$ | concentration of gaseous $H_2O$ (molecules m$^{-3}$) |
| $n_d$ | acid droplet number concentration (droplets cm$^{-3}$) |
| $n_p$ | nuclei particle number concentration (particles cm$^{-3}$) |
| $P_{H_2SO_4}$ | equilibrium partial pressure of $H_2SO_4$ over liquid acid (mm Hg) |
| $P$ | total pressure |
| $p_a$ | partial pressure of $H_2SO_4$ in bulk stack gases |
| $p_{as}$ | partial pressure of $H_2SO_4$ at the surface of acid droplet |
| $p_r$ | vapor pressure of drop of radius $r$ |
| $p_\infty$ | vapor pressure of flat liquid surface |
| $Q_E$ | light extinction efficiency factor |
| $r$ | particle radius (cm) |
| $R$ | gas constant |
| $T$ | temperature (K) |
| $T_i$ | temperature of initial stack gas |
| $t_{1/2}$ | time for $\frac{1}{2}$ of aerosol to coagulate |
| $T_{dp}$ | temperature of dewpoint of sulfuric acid (K) |
| $V_{acid}$ | volume sulfuric acid/particle (cm$^3$ particle$^{-1}$) |
| $W$ | total particle mass concentration (g m$^{-3}$) |
| $X_a$ | weight fraction $H_2SO_4$ in liquid sulfuric acid |

*Greek symbols*

| | |
|---|---|
| $\lambda$ | wavelength of light ($\mu$m) |
| $\rho$ | density of particle (g cm$^{-3}$) |
| $\rho_a$ | density of acid |
| $\beta_{acid}$ | $H_2SO_4$ molecular impingement rate (molecules cm$^{-2}$ s$^{-1}$) |
| $\sigma^*$ | surface tension of embryo nucleus droplet (dyne cm) |
| $\Phi_{H_2SO_4}$ | $H_2SO_4$ molecular flux (molecules nuclei$^{-1}$ s$^{-1}$) |
| $\tau$ | time for depletion of $H_2SO_4$ vapor (s) |
| $\tau_{nuc}$ | time for $H_2SO_4$ vapor depletion by nucleation (s) |
| $\tau_{cond}$ | time for $H_2SO_4$ vapor depletion by heterogeneous condensation (s). |

## 1. INTRODUCTION

### (A) *Effect of sulfuric acid on opacity*

Plume opacity may be significantly affected by the condensation of sulfuric acid vapors in stack gas emissions. Nader and Conner (1978) reported that the out-stack opacity of emissions from oil-fired boilers increased with increasing sulfuric acid concentrations, whereas the in-stack opacity was not affected. They reasoned that the in-stack gases are at a temperature above the sulfuric acid dewpoint (at about 150°C) and thus at the hotter in-stack conditions the opacity is not influenced by the sulfuric acid concentration. However, the sulfuric acid vapors cool upon leaving the stack and condense, forming dilute sulfuric acid droplets (about 70% $H_2SO_4$ and 30% $H_2O$ by weight). Nader and Conner (1978) concluded that the increased opacity of the out-stack gases compared to the in-stack gases was probably caused by the condensation of the sulfuric acid vapors.

The maximum allowable plume opacity is regulated in many countries and thus the effects of condensed sulfuric acid vapors, absorbed water vapor (uncombined water), the nuclei particle size distribution, and the nuclei particle mass concentration on the observed out-stack opacity are of interest. Some air pollution control regulations allow the contribution of uncombined water (water not chemically bound to the aerosol particles) to the opacity to be subtracted from the observed out-stack opacity. The removal of the effects of the uncombined water from the observed opacity is not easily done. One method is for the smoke inspector to read the plume opacity at a point downwind in the plume where the water was evaporated (procedure can be used with stack gases emitted from a wet scrubber and when the atmospheric air temperature and humidity enables the water to evaporate). However, this is not a satisfactory procedure for smoke plumes containing aerosol droplets of hygroscopic solutions (such as sulfuric acid) in which the water does not evaporate readily.

### (B) *Purpose of paper*

The purpose of this paper is to present the calculated opacities and calculated final sulfuric acid droplet diameters as a function of the stack gas initial $H_2SO_4$ concentration, initial water vapor concentration, condensation nuclei concentration and final temperature. The calculations presented consider the cooling of the stack gases from 300–30°C without the dilution with atmospheric air (cooling without the dilution of the stack gases is the worst case with regards to the largest opacity magnitude). The results of this paper have significance in explaining, in general, the effects of the initial concentrations of water vapor and sulfuric acid and the final gas temperature on the opacity, which air pollution control regulations usually limit to a maximum allowable in the 20–40% range. Sources emitting gases containing sulfuric acid in vapor and/or droplet form include oil-fired boilers, oil refineries, metal smelters and sulfuric acid plants.

### (C) *Literature review*

Opacity is related to the fraction of light transmitted through a plume, $I/I_0$ by

$$\mathrm{Op} = 1 - I/I_0, \tag{1}$$

where Op is the fraction of light obscured. Measured and calculated optical properties and visual effects of plumes have been studied by Conner and Hodkinson (1967). The relationship of the opacity to the particle mass concentration, particle size distribution, particle refractive index and plume dimensions has been reported by Pilat and Ensor (1970a), Larssen *et al.* (1972) and Thielke and Pilat (1978).

Sulfuric acid aerosols have been studied extensively. LaMer *et al.* (1950) reported that the nucleation of sulfuric acid aerosols could be controlled only when the nuclei number concentration exceeded the number concentration formed by self-nucleation of the $H_2SO_4$ vapor. This concentration was $10^6$ cm$^{-3}$. Gillespie and Johnstone (1955) reported that $H_2SO_4$ vaporized at 225°C from 98% $H_2SO_4$, upon cooling formed an aerosol of number concentration $10^3$ cm$^{-3}$ by self-nucleation. The $H_2SO_4$ aerosol had mass mean diameters in the 0.45–1.1 $\mu$m range. Nair and Vohra (1975) presented computed diameters of sulfuric acid droplets at equilibrium in the 0–110% relative humidity range for initial dry $H_2SO_4$ droplets of 0.001–0.5 $\mu$m diameter. Hamill (1975) presented a theory for heteromolecular condensation of $H_2O$ and $H_2SO_4$ to form sulfuric acid droplets. Hamill pointed out that the larger droplets (dia. $> 0.05\ \mu$m) grow faster than the smaller droplets (dia. $< 0.001\ \mu$m) because the lower required acid molality for equilibrium of the larger droplets allows more water vapor to be absorbed. Yue (1979) reported a quick method for estimating the equilibrium size and composition of aqueous sulfuric acid droplets. This method applies to the homogeneous heteromolecular nucleation and condensation of $H_2O$ and $H_2SO_4$.

## 2. MECHANISMS OF SULFURIC ACID CONDENSATION

### (A) *Condensation*

Two possible mechanisms of sulfuric acid condensation in stack gases are

(1) Homogeneous heteromolecular nucleation of gaseous $H_2O$ and $H_2SO_4$ molecules to form very small (5–20 Angstroms diameter) dilute sulfuric acid droplets.

(2) Heterogeneous heteromolecular condensation of gaseous $H_2O$ and $H_2SO_4$ molecules onto solid nuclei particles to form droplets of dilute sulfuric acid coating the nuclei particles.

The ultimate size distribution of the sulfuric acid droplets is dependent upon the condensation mechanism occurring to convert the gaseous $H_2O$ and $H_2SO_4$ into dilute sulfuric acid liquid and upon the amount of coagulation of the droplets. A comparison of the rates of homogeneous nucleation and heterogeneous condensation will show the mechanism expected to dominate in industrial stack gases. Typical stack gas emissions from fossil fuel fired boilers have 5–15% by volume water vapor, 1–30 ppm $H_2SO_4$, 0.001–0.05 grains/acf (0.00229–0.1144 g m$^{-3}$) particle mass concentration, $10^6$–$10^8$ particles cm$^{-3}$ particle number concentration and 80–200°C gas temperatures.

### (B) *Homogeneous nucleation*

The homogeneous nucleation of sulfuric acid can be assumed to be limited by the impingement rate of $H_2SO_4$ molecules because the $H_2O$ concentration far exceeds the $H_2SO_4$ concentration in industrial stack gases. The calculation of the nucleation rate and the nucleation rate time constant (time required to condense all the initially present $H_2SO_4$ vapor) will illustrate the significance of homogeneous nucleation.

Kiang and Stauffer (1973) reported a calculation procedure for the nucleation rate $J$ as a function of the water vapor and sulfuric acid vapor concentrations and the diameter of the nucleated droplet.

$$J = 4\pi r^{*2}\,(\beta_{\text{acid}})\,n_w \exp\left(-\frac{\Delta G^*}{kT}\right), \qquad (2)$$

where $r^*$ is the radius of the embryo nucleus sulfuric acid droplet, $\beta_{\text{acid}}$ the $H_2SO_4$ molecule impingement rate, $n_w$ the $H_2O$ molecular gas concentration, $\Delta G^*$ the free energy of formation of the embryo nuclei droplet from gaseous water vapor and sulfuric acid vapor, $k$ the Boltzmann's constant and $T$ the gas temperature. The sulfuric acid impingement rate is given by

$$\beta_{\text{acid}} = \frac{n_a kT (N_{\text{av}})^{1/2}}{(2\pi M_{H_2SO_4} kT)^{1/2}}, \qquad (3)$$

where $n_a$ is the gaseous sulfuric acid molecular concentration, $M_{H_2SO_4}$ the $H_2SO_4$ molecular weight and $N_{\text{av}}$ Avogadro's constant. The free energy increase of formation of the embryo nuclei droplet is given by

$$\Delta G^* = \tfrac{4}{3}\pi \sigma^* r^{*2}, \qquad (4)$$

where $\sigma^*$ is the surface tension of the embryo nucleus sulfuric acid droplet.

The droplet nucleation rate $J$ was calculated for gas temperatures of 50, 100 and 150°C in the 1–1000 ppm $H_2SO_4$ concentration range, and at 5% water vapor using equation (2) and the results are presented in Fig. 1. The homogeneous nucleation rate is highly dependent upon both the $H_2SO_4$ vapor phase concentration and the gas temperature. At 100°C and $H_2SO_4$ concentrations of below 10 ppm the nucleation rate is calculated to be about 1 droplet cm$^3$ s$^{-1}$, which is a rather insignificant rate.

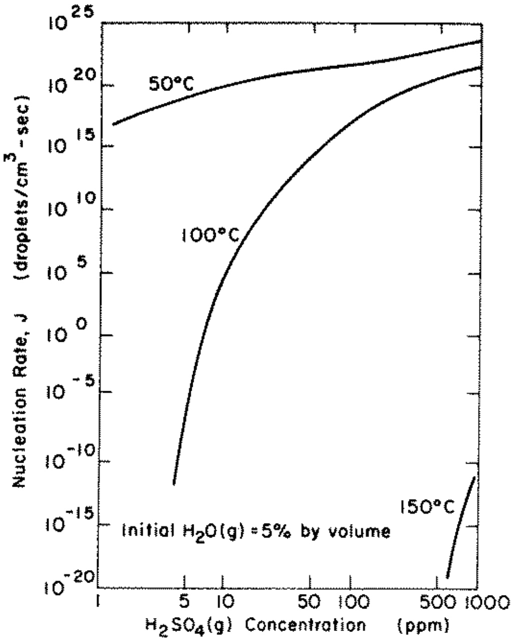

Fig. 1. Calculated homogeneous nucleation rate.

### (C) *Heterogeneous condensation*

Heterogeneous heteromolecular condensation of gaseous $H_2O$ and $H_2SO_4$ onto solid nuclei particles forming dilute sulfuric acid liquid surrounding the nuclei occurs when there are sufficient nuclei and when both gaseous $H_2O$ and $H_2SO_4$ are supersaturated with respect to the liquid dilute sulfuric acid. The sulfuric acid condensation rate can be assumed to be limited entirely by the $H_2SO_4$ impingement rate because of the excess concentration of $H_2O$ vapor. Assuming the sulfuric acid condensation rate is limited by the vapor-phase diffusion to the particle surface, as reported by Hamill (1975) and Carabine and Maddock (1976), the droplet growth rate can be estimated from the $H_2SO_4$ molecular flux to the droplet surface. Using Maxwell's equation the $H_2SO_4$ molecular flux to the drop surface is given by

$$\Phi_{H_2SO_4} = \frac{4\pi r D_{H_2SO_4} M_{H_2SO_4}}{RT}\,(p_{a\infty} - p_{as}) \qquad (5)$$

where $\Phi_{H_2SO_4}$ is the $H_2SO_4$ molecular flux onto a particle of radius $r$, $D_{H_2SO_4}$ is the diffusivity of $H_2SO_4$ in the stack gases, $p_{a\infty}$ the partial pressure of $H_2SO_4$ in the bulk stack gases and $p_{as}$ the partial pressure of $H_2SO_4$ at the droplet surface. For small droplets, the vapor pressure over a curved liquid surface is greater than over a flat surface. The Kelvin–Gibbs equation is

$$\ln\left(\frac{p_r}{p_\infty}\right) = \frac{2M_a\sigma}{RT\rho_a \cdot r}, \qquad (6)$$

where $p_\infty$ is the equilibrium vapor pressure for a flat liquid surface, $p_r$ the vapor pressure of the drop of radius $r$, $M_a$ the acid molecular weight, $\sigma$ the liquid surface tension and $\rho_a$ the acid density. Using an acid density of 1.4 g cm$^{-3}$ from Perry (1973), an acid surface tension of 65 dynes cm$^{-1}$ from Timmermans (1960), an acid molecular weight of 35.2 g gmole$^{-1}$, and a gas temperature of 100°C the vapor pressure correction amounts to 16% for a 0.01 μm diameter and only 6% for a 0.05 μm dia. Because the vapor pressure correction is of a magnitude that is probably less than the uncertainty in the $H_2SO_4$ vapor pressure at temperatures other than 25°C, the effect of the droplet curvature is assumed to be insignificant for this paper.

The $H_2SO_4$ molecular flux, calculated with equation (5) for nuclei particles of 0.05 $\mu$m diameter, a nuclei concentration of $5 \times 10^7$ particles cm$^{-3}$, water vapor concentration of 5 and 10% and in the 1–1000 ppm $H_2SO_4$ range is shown in Fig. 2.

### (D) *Comparison of nucleation and condensation rates*

The relative rates of heterogeneous condensation vs homogeneous nucleation can be quantitatively compared, by developing reaction time constants similar to those used by Stauffer *et al.* (1973). The time constant for either process is defined as the specified $H_2SO_4(g)$ concentration, divided by the instantaneous rate of acid vapor removal:

$$\tau(\mathrm{s}) = \frac{\text{initial } H_2SO_4(g) \text{ vapor concentration}}{H_2SO_4 \text{ vapor depletion rate}} \tag{7}$$

$$\tau_{\mathrm{cond}} = \frac{n_a(\text{molecules } H_2SO_4\,\mathrm{cm}^{-3})}{\Phi\left(\dfrac{\text{molecules}}{\text{nuclei-s}}\right) n_p(\text{particles cm}^{-3})} \tag{8}$$

$$\tau_{\mathrm{nuc}} = \frac{n_a(\text{molecules } H_2SO_4\,\mathrm{cm}^{-3})}{J\left(\dfrac{\text{droplets}}{\mathrm{cm}^3\text{-s}}\right)\left[\dfrac{4\pi}{3} r^{*3} \rho_a^* \chi_4^* N_{AV} \dfrac{1}{M_{H_2SO_4}}\right]}. \tag{9}$$

These time constants do not actually represent the total time required to deplete all supersaturated acid vapors from the gas stream. Instead, they represent the instantaneous vapor depletion rate, at any specified vapor concentration and temperature conditions. The relative importance of condensation vs nucleation at any specified conditions is thus determined by the ratio of the time constants $\tau_{\mathrm{cond}}/\tau_{\mathrm{nuc}}$. If the ratio is much greater than unity, then nucleation is much faster than condensation under the specified conditions, so nucleation should be the dominant acid droplet formation/growth mechanism. If the time constant ratio is much smaller than unity, then condensation onto existing particles should be dominant mechanism for depleting supersaturated acid vapors.

The calculated ratios $\tau_{\mathrm{cond}}/\tau_{\mathrm{nuc}}$ for different temperatures and sulfuric acid vapor concentrations are shown in Fig. 4. The assumed values for water vapor concentration and condensation nucleus concen-

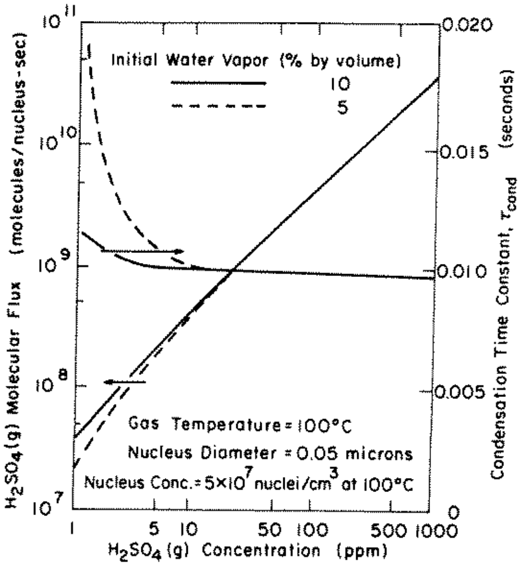

Fig. 2. Calculated $H_2SO_4$ molecular flux to nuclei particle.

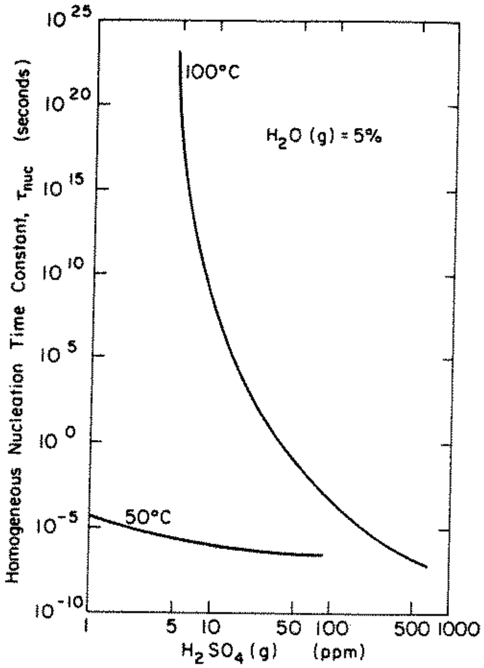

Fig. 3. Calculated homogeneous nucleation time constants.

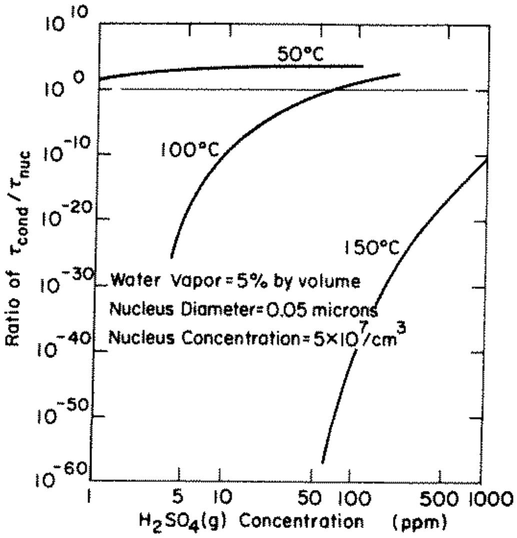

Fig. 4. Comparison of nucleation and condensation time constants.

tration represent values commonly measured in industrial air pollution emissions. The calculated time constant ratio decreases by many orders of magnitude with increasing gas temperature, from 50 to 150°C. The ratio increases with higher sulfuric acid vapor concentration. From this figure, it appears that for any specified acid vapor concentration, homogeneous nucleation should dominate at low temperature (below 50°C), while heterogeneous condensation should dominate at temperatures above roughly 100°C.

However, by considering the processes by which industrial emissions are cooled, it can confidently be shown that condensation onto existing particles should always be the dominant mechanism for depletion of supersaturated acid vapors in cooling industrial emissions. Consider for example, an emission stream at 150°C containing 10 ppm sulfuric acid vapors. By the acid dewpoint correlations of Banchero and Verhoff (1975), the dewpoint temperature at 5% water vapor and 10 ppm acid vapor is roughly 130°C, so no acid droplet formation should occur until the emissions are cooled to below that temperature. According to Fig. 4, when droplet formation does occur at 130°C, condensation onto the existing particles should be the dominant vapor depletion mechanism. Next, assume that emission cooling continues over a period of seconds, until the emission temperature is 75°C, with vapor/liquid equilibrium approached at all times during the cooling process. By the dewpoint correlations, the equilibrium acid vapor concentration at that temperature should be below 0.1 ppm. From Fig. 4, it appears that condensation onto existing particles will still be the dominant droplet growth mechanism.

By this same reasoning, it is seen that if emission cooling is slow enough so that vapor/liquid equilibrium is approached at all times, then the equilibrium acid vapor concentration should always be maintained at levels well below that for which homogeneous nucleation becomes an important droplet formation mechanism. It thus appears that heterogeneous condensation of acid vapors onto existing particles should usually be the dominant droplet formation mechanism in cooling industrial emissions.

Of course, this does not imply that nucleation of new acid droplets will never occur in cooled emissions. If the cooling rate proceeds much faster than does the condensation rate, then the surfuric acid vapor supersaturation will become high enough for nucleation to occur at any temperature. Many researchers have used electrostatic aerosol size analyzers and/or diffusion batteries equipped with CCN counters, to attempt to measure ultrafine particle size distributions in industrial emissions. They have found that all sulfuric acid vapors must be removed from the gas stream before the CCN counter is used for particle counting, or nucleation of acid droplets in the CCN counter can give erroneously high results. However, the supersaturations created in a CCN counter are much higher than those expected in a cooling emission stream.

## 3. SULFURIC ACID PROPERTIES

### (A) *Vapor pressures*

Gmitro and Vermeulen (1964) reported an equation for the vapor pressure of $H_2SO_4$ over sulfuric acid with coefficients which are functions of the acid composition, partial molar heat capacity, free energy and enthalpy of water and sulfuric acid. Because these coefficients are difficult to determine, for the calculations in this paper simple expressions for $p_{H_2O}$ and $p_{H_2SO_4}$ were developed based on either log-linear or log-parabolic graphical curves that fit the data of Gmitro and Vermeulen.

$$\log_{10} p_{H_2O} = AX_a^2 + BX_a + C \qquad (10)$$

$$\log_{10} p_{H_2SO_4} = EX_a + F, \qquad (11)$$

where $p_{H_2O}$ and $p_{H_2SO_4}$ are in mm Hg, $X_a$ is the weight fraction $H_2SO_4$ in the condensed liquid dilute sulfuric acid and the coefficients $A$, $B$, $C$, $E$ and $F$ are functions of temperature and $X_a$. Figure 5 presents the vapor pressure curves for $H_2O$ and Fig. 6 the vapor pressure curves for $H_2SO_4$ as a function of the weight fraction $H_2SO_4$ in the liquid sulfuric acid and at various temperatures.

### (B) *Density*

The density of liquid sulfuric acid as a function of temperature and composition was obtained from data reported by Timmermans (1960) and Perry (1973). The sulfuric acid density was approximated with a linear equation

$$\rho_a = 0.75X_a + 1.0, \qquad (12)$$

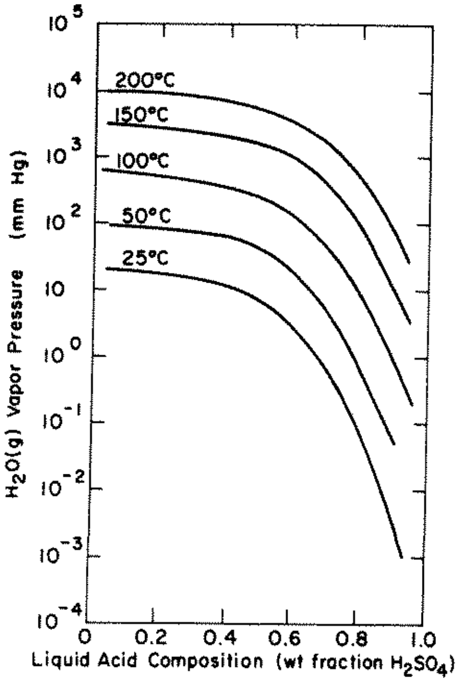

Fig. 5. $H_2O$ vapor pressure vs acid composition.

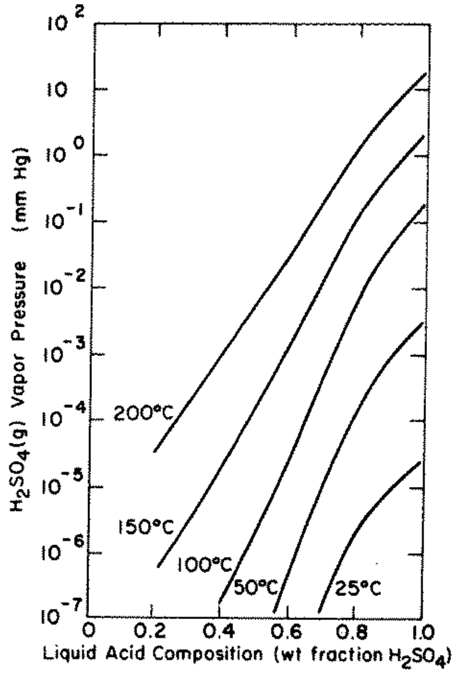

Fig. 6. $H_2SO_4$ vapor pressure vs acid composition.

where $\rho_a$ is the sulfuric acid density and $X_a$ the weight fraction $H_2SO_4$ in the liquid sulfuric acid.

## 4. CALCULATIONS OF DROPLET DIAMETER

### (A) *Size of acid droplets*

A model of monodisperse solid particle nuclei of 0.05 $\mu$m diameter with heterogeneous condensation of the sulfuric acid vapors onto these nuclei was used to calculate the resultant droplet diameters and opacities as a function of initial sulfuric acid concentration, initial water vapor concentration and final gas temperature. Nuclei concentrations of $10^6$–$10^8$ cm$^{-3}$ were used. The stack gases were assumed to initially be at 300°C and atmospheric pressure. With a decrease in the stack gas temperature, the gases cool to the sulfuric acid dewpoint and the vapors are assumed to condense only on the nuclei. The cooling is assumed to occur with no dilution of the stack gases and thus this is a worst case situation regarding the size of the droplets and the calculated opacity (maximums). The assumed nuclei particle number concentrations in the $10^6$–$10^8$ cm$^{-3}$ are in the range reported in the literature. McCain (1978) reported particle concentrations of $4 \times 10^7$ cm$^{-3}$ at the outlet of a venturi scrubber at a coal-fired power plant (measured with TSI Electrical Aerosol Analyzer and Royco optical particle counter). Calvert (1977) reported that industrial emissions have particle number concentrations of the order of $10^6$–$10^8$ cm$^{-3}$.

The diameter of the sulfuric acid droplets after condensation of the $H_2SO_4$ and $H_2O$ vapors onto the nuclei particles is obtained by volume balance. The volume of sulfuric acid condensed onto each nucleus particle is given by

$$V_{acid}(\text{cm}^3\ \text{particle}^{-1}) = V_{droplet} - V_{nucleus} \tag{13}$$

$$V_{acid} = \frac{\pi}{6}(D^3 - d^3), \tag{14}$$

where $D$ is the acid droplet diameter and $d$ is the nucleus diameter. Solving for the droplet diameter $D$

$$D = \left(\frac{6}{\pi} V_{acid} + d^3\right)^{1/3}. \tag{15}$$

Relating the volume of acid condensed on each particle to the mass of acid per particle $W_{acid}$

$$V_{acid}\left(\frac{\text{cm}^3\ \text{acid}}{\text{particle}}\right) = \frac{W_{acid}(\text{g acid particle}^{-1})}{\rho_a(\text{g acid cm}^{-3}\ \text{acid})}. \tag{16}$$

The acid density $\rho_a$ is related to the weight fraction $H_2SO_4$ in the dilute sulfuric acid by equation (12). Substituting equation (16) for $V_{acid}$ into equation (15) gives

$$D = \left(\frac{6W_{acid}}{\pi\rho_a} + d^3\right)^{1/3}. \tag{17}$$

The mass of acid per particle $W_{acid}$ is related to the liquid acid concentration $m_{acid\ liquid}$ (g acid m$^{-3}$) by

$$W_{acid}\left(\frac{\text{g acid}}{\text{particle}}\right) = \frac{m_{acid\ liquid}(\text{g acid m}^{-3})}{N\ (\text{particles m}^{-3})}, \tag{18}$$

where $N$ is the particle number concentration. Substituting for the acid liquid concentration $M_{acid}$ in (17) gives

$$D = \left(\frac{6m_{acid\ liquid}}{\pi\rho_a N} + d^3\right)^{1/3}. \tag{19}$$

### (B) *Condensed sulfuric acid*

The concentration of condensed sulfuric acid $M_{acid}$ was calculated using $H_2O$ and $H_2SO_4$ mass balances. The amount of sulfuric acid condensed is dependent upon the initial water vapor and sulfuric acid vapor concentrations and the final temperature. The mass balances on the $H_2O$ and $H_2SO_4$ are

$$m_{H_2O\ Total}\left(\frac{\text{g H}_2\text{O}}{m^3}\right) = m_{H_2O\ Final\ vapor} + m_{H_2O\ Liquid} \tag{20}$$

$$m_{H_2SO_4\ Total}\left(\frac{\text{g H}_2\text{SO}_4}{m^3}\right) = m_{H_2SO_4\ Final\ vapor} + m_{H_2SO_4\ Liquid}, \tag{21}$$

where $m_{H_2O}$ and $m_{H_2SO_4}$ are the mass concentrations of $H_2O$ and $H_2SO_4$ in units of g m$^{-3}$ at 300°C and 1 atmosphere pressure, and these were calculated from ideal gas laws

$$m_{H_2O\ Total} = \frac{C_{i\,H_2O} P M_{H_2O}}{10^6 RT_i} \tag{22}$$

$$m_{H_2SO_4\ Total} = \frac{C_{i\,H_2SO_4} P M_{H_2SO_4}}{10^6 RT_i}, \tag{23}$$

where $T_i$ is the initial stack gas temperature (300°C), $R$ the gas constant, $P$ the total pressure (1 atmosphere), $M_{H_2O}$ the water molecular weight, $M_{H_2SO_4}$ the sulfuric acid molecular weight, $C_{iH_2O}$ and $C_{iH_2SO_4}$ the initial vapor concentrations (ppm) of water and sulfuric acid, respectively.

The final vapor concentrations for water and sulfuric acid at conditions below the acid dewpoint were calculated using the ideal gas laws and the partial pressures of $H_2O$ and $H_2SO_4$ at temperature and acid composition of the condensed acid

$$m_{H_2O\ \text{Final Vapor}}(\text{g } H_2O \text{ m}^{-3}) = \frac{p_{H_2O}M_{H_2O}}{RT_i} \tag{24}$$

$$m_{H_2SO_4\ \text{Final Vapor}}(\text{g } H_2SO_4 \text{ m}^{-3}) = \frac{p_{H_2SO_4}M_{H_2SO_4}}{RT_i}, \tag{25}$$

where $p_{H_2O}$ and $p_{H_2SO_4}$ are the equilibrium vapor pressures for $H_2O$ and $H_2SO_4$ over the condensed sulfuric acid, and were calculated using equations (10) and (11), respectively. $m_{H_2O}$ liquid and $m_{H_2SO_4}$, the concentrations of $H_2O$ and $H_2SO_4$ in the condensed acid liquid, were calculated by solving the equations

$$m_{H_2O\ \text{Liquid}} = \frac{(C_i - C_f)_{H_2O}}{10^6}\,\frac{PM_{H_2O}}{RT_i} \tag{26}$$

$$m_{H_2SO_4\ \text{Liquid}} = \frac{(C_i - C_f)_{H_2SO_4}}{10^6}\,\frac{PM_{H_2SO_4}}{RT_i}. \tag{27}$$

The mass concentration of condensed dilute sulfuric acid is related to the concentrations of $H_2SO_4$ and $H_2O$ by

$$m_{\text{acid Liquid}} = \frac{m_{H_2SO_4\ \text{Liquid}}(\text{grams } H_2SO_4 \text{ m}^{-3})}{X_a(\text{g } H_2SO_4 \text{ g}^{-1} \text{ acid})} \tag{28}$$

$$m_{\text{acid Liquid}} = \frac{m_{H_2O\ \text{Liquid}}(\text{g } H_2O \text{ m}^{-3})}{(1 - X_a)(\text{g } H_2O \text{ g}^{-1} \text{ acid})}. \tag{29}$$

Equating (27) and (28) and solving for $m_{H_2SO_4\ \text{Liquid}}$ gives

$$m_{H_2SO_4\ \text{Liquid}} = \frac{m_{H_2O\ \text{Liquid}}X_a}{(1 - X_a)}. \tag{30}$$

Substituting (26) for $m_{H_2O\ \text{Liquid}}$ in (29) gives

$$m_{H_2SO_4\ \text{Liquid}} = \frac{(C_i - C_f)_{H_2O}}{10^6}\,\frac{PM_{H_2O}X_a}{RT_i(1 - X_a)}. \tag{31}$$

Substituting (23) for $m_{H_2SO_4\ \text{Total}}$ (24) for $m_{H_2SO_4\ \text{Final Vapor}}$ and (31) for $m_{H_2SO_4\ \text{Liquid}}$ into the overall $H_2SO_4$ mass balance, (21) gives

$$\frac{C_{i\,H_2SO_4}PM_{H_2SO_4}}{10^6\,RT_i} = \frac{P_{H_2SO_4}M_{H_2SO_4}}{RT_i} + \frac{(C_i - C_f)_{H_2O}PM_{H_2O}X_a}{10^6\,RT_i(1 - X_a)}. \tag{32}$$

Simplifying (32) by cancellation and rearrangement

$$\frac{C_{i\,H_2SO_4}}{10^6} = \frac{P_{H_2SO_4}}{P} + \frac{(C_i - C_f)_{H_2O}M_{H_2O}X_a}{10^6\,M_{H_2SO_4}(1 - X_a)}. \tag{33}$$

For given conditions of the initial $H_2O$ and $H_2SO_4$ vapor concentrations and the final temperature of the cooled stack gases, there are three unknowns in Equation (33); the vapor pressure of $H_2SO_4$ ($p_{H_2SO_4}$), the final concentration of water vapor ($C_{f\,H_2O}$), and the condensed acid concentration ($X_a$). The $H_2O$ and $H_2SO_4$ vapor pressures are related to the acid compositions by (10) and (11), respectively. The liquid acid compositions $X_a$ for various initial concentrations and final temperatures were calculated using numerical computation techniques (digital computer). These calculations also provided the final $H_2O$ and $H_2SO_4$ vapor concentrations (from (10) and (11)) and the acid density (12).

Equations (31) and (28) were used to calculate the amount of dilute sulfuric acid liquid condensed. Equation (19) with the dilute sulfuric acid liquid concentration provided the acid droplet diameter.

## 5. OPACITY CALCULATIONS

The opacity was calculated for a plume diameter of 6 m, a particle refractive index of 1.43, and light of wavelength 0.55 μm. Light of this wavelength is in the range of highest human eye sensitivity. Pilat and Ensor (1970a) reported a general relationship between the light transmittance through a plume $I/I_0$, the plume diameter or light pathlength through the plume $L$ and the particle properties (particle size distribution, particle density, particle mass concentration and particle refractive index). The general equation reported by Pilat and Ensor is in the form of the Bouguer Law (Beer–Lambert Law)

$$I/I_0 = -\frac{WL}{K\rho}, \tag{34}$$

where $W$ is the total aerosol particle mass concentration, $\rho$ is the particle density and $K$ is the specific particle volume light extinction coefficient ratio. $K$ is given as

$$K = \frac{W}{\rho B_E}, \tag{35}$$

where $B_E$ is the light extinction coefficient. The light extinction coefficient for a polydisperse aerosol is given by

$$B_E = \int_0^\infty Q_E(r, \lambda, m)\pi r^2 n(r)\,dr, \tag{36}$$

where $Q_E$ is the light extinction efficiency factor and $n(r)$, the particle number frequency distribution. In this paper the particles are monodisperse and thus $n(r) = N$, the total particle number concentration.

The opacity calculations were performed by computer and the Mie equations, as reported by Van de Hulst (1957) or Kerker (1969).

## 6. RESULTS

### (A) *Calculated droplet diameters*

The sulfuric acid droplet diameters at final gas temperatures of 70, 100 and 125°C; initial stack gas water vapor concentrations of 1 and 10% by volume; nuclei number concentration of $10^6$ $cm^{-3}$ (gas volume at 300°C) and cooled from 300°C are presented in Fig. 7 as a function of the initial $H_2SO_4$ concentration. At 300°C all of the $H_2SO_4$ was in the vapor phase. In general Fig. 7 shows that the both higher initial water vapor and initial $H_2SO_4$ concentrations result in larger final acid droplet diameters. Calculations at nuclei concentrations of $10^7$ and $10^8$ $cm^{-3}$ showed similar effects except that the higher nuclei concentrations result in smaller acid droplet diameters at the final gas temperature.

Figure 8 shows the acid droplet diameter as a function of the final gas temperature at initial $H_2SO_4$ concentrations of 5, 20 and 70 ppm; initial water vapor concentrations of 1 and 10% by volume; nuclei concentration of $10^6$ $cm^{-3}$, and cooled from an initial temperature of 300°C. In general Fig. 8 shows that:

(1) The sulfuric acid dewpoint is a function of both the initial $H_2O$ vapor and the $H_2SO_4$ concentrations.

(2) Upon cooling from 300°C, the particle diameter remains at 0.05 μm until the sulfuric acid begins to condense.

(3) With further cooling below the sulfuric acid dewpoint, the diameter increases substantially for about 15°C below the acid dewpoint by mainly $H_2SO_4$ condensation.

(4) The droplet diameter remains fairly constant with further cooling until the water dewpoint ($H_2O$ dewpoint assuming no hygroscopic substances like sulfuric acid are present) is reached.

(5) At the water vapor dewpoint, the droplet diameter increases greatly.

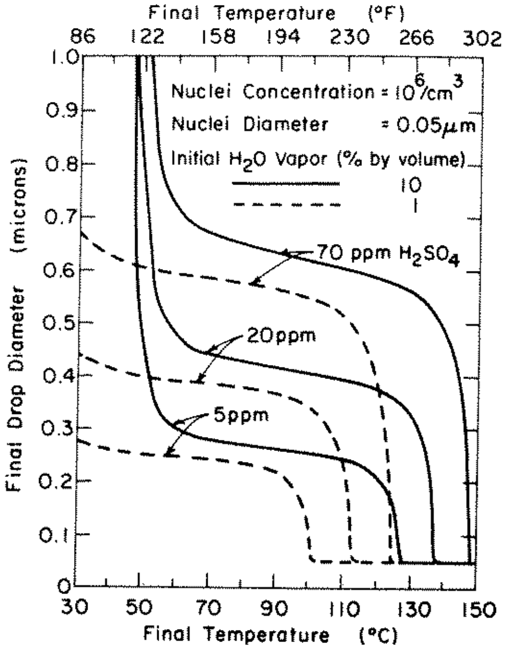

Fig. 8. Droplet diameter as function of final gas temperature.

### (B) *Calculated opacities*

The opacities were calculated for a stack diameter of 6 m, atmospheric pressure of 760 mm Hg and stack gases cooled from 300°C are presented in Figs 9–

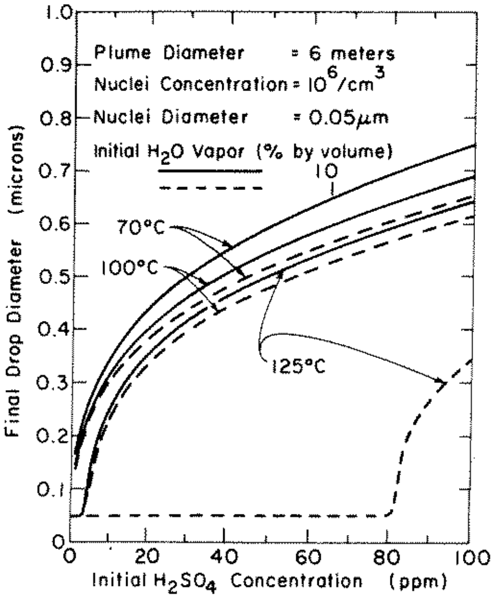

Fig. 7. Droplet diameter as function of initial $H_2SO_4$ concentration.

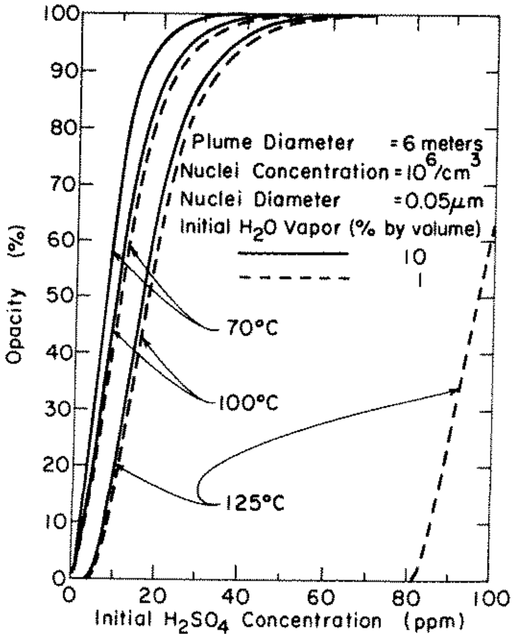

Fig. 9. Opacity as function of $H_2SO_4$ at $10^6$ nuclei $cm^{-3}$

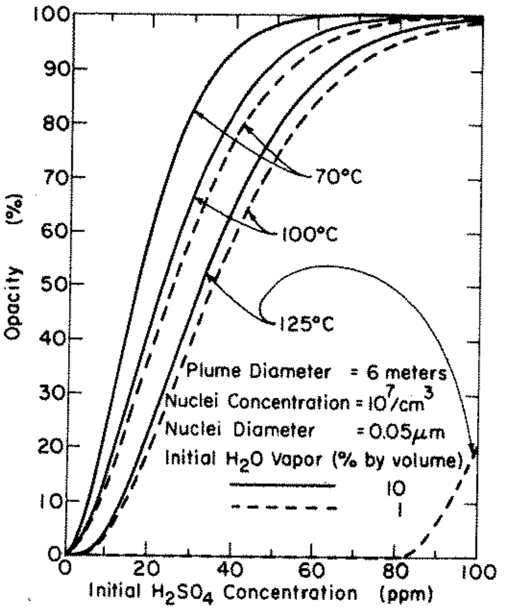

Fig. 10. Opacity as function of $H_2SO_4$ at $10^7$ nuclei $cm^{-3}$.

11 as a function of the initial $H_2SO_4$ concentration and Figs 12–14 as a function of the final gas temperature. The nuclei concentrations are $10^6$, $10^7$ and $10^8$ $cm^{-3}$ for Figs 9, 10 and 11, respectively, and for Figs 12, 13 and 14, respectively.

Figures 9–11 show that the calculated opacities:

(1) increase substantially with increases in the initial $H_2SO_4$ concentration;

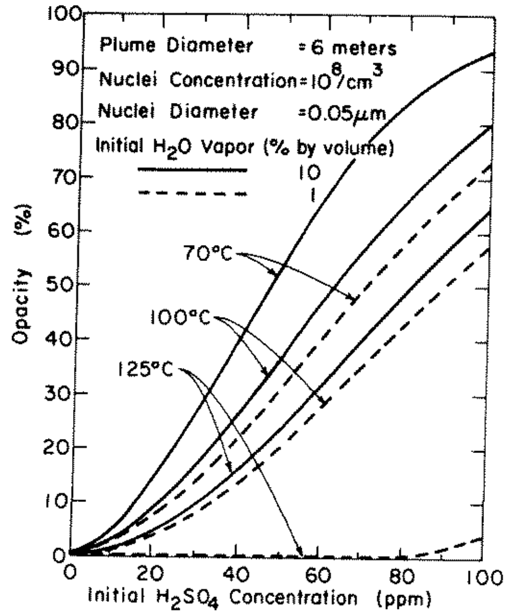

Fig. 11. Opacity as function of $H_2SO_4$ at $10^8$ nuclei $cm^{-3}$.

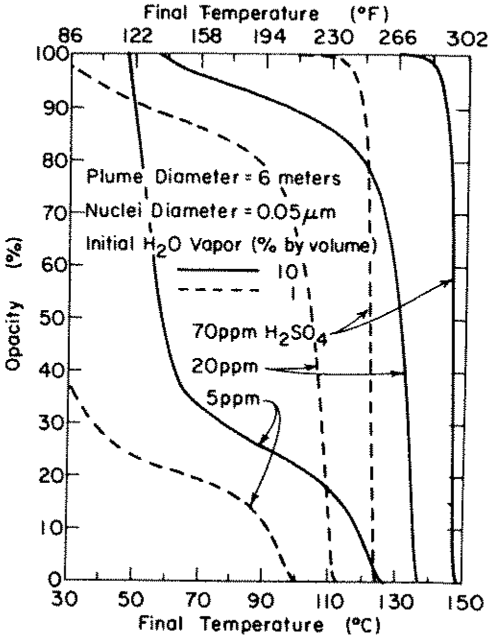

Fig. 12. Opacity as function of final temperature at $10^6$ nuclei $cm^{-3}$.

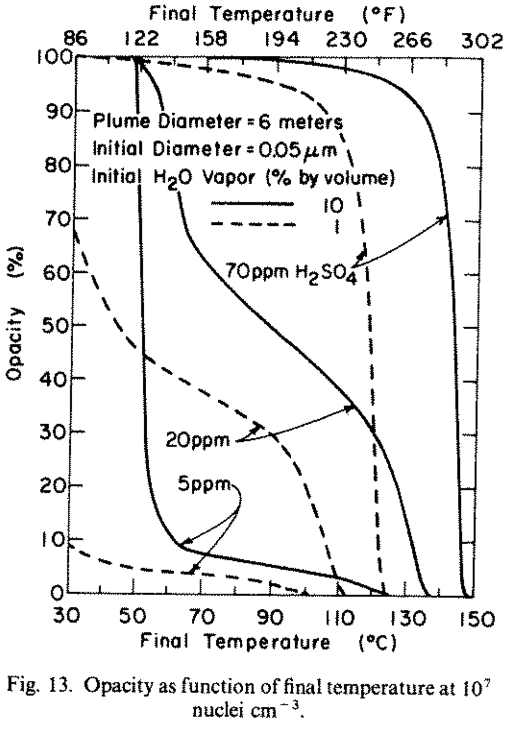

Fig. 13. Opacity as function of final temperature at $10^7$ nuclei $cm^{-3}$.

(2) increases somewhat with increasing initial $H_2O$ concentration and

(3) decreases with increasing nuclei number concentration.

The smaller nuclei particle number concentration results in larger acid droplet diameters, which in the active light extinction particle size range (particle radii

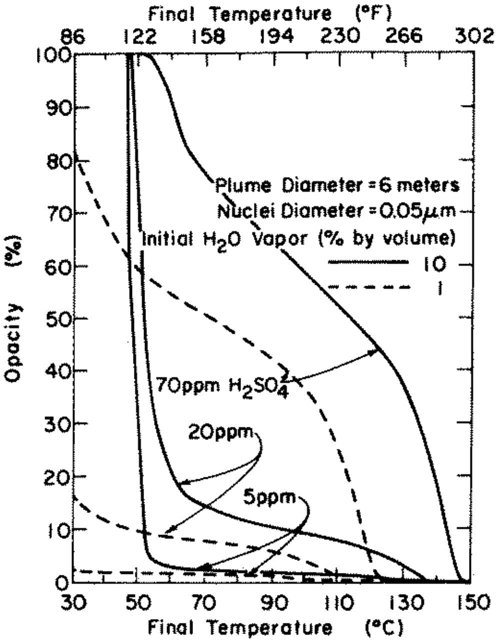

Fig. 14. Opacity as function of final temperature at $10^8$ nuclei $cm^{-3}$.

just smaller than the wavelength of light used in the calculations, 0.55 $\mu m$) produce large opacities. The particle mass concentration/light extinction coefficient ratio goes through a minimum at a particle diameter of about 1.0 $\mu m$ (this depends somewhat on the particle refractive index). The acid droplet diameters formed with the $10^6$ $cm^{-3}$ nuclei concentration are in a range where the magnitude of the particle mass concentration/light extinction coefficient ratio is smaller than for the $10^8$ $cm^{-3}$ nuclei concentration, and hence the opacities calculated for the $10^6$ $cm^{-3}$ nuclei concentration are larger even though the amount of condensed liquid sulfuric acid is identical. Thus with droplet diameters calculated for this paper being less than 1.0 $\mu m$ at the final gas temperature above 60°C, the larger droplets are efficient in the extinction of light. And the lower nuclei concentrations give the larger droplet diameters and accordingly the larger opacities for a specific amount of acid condensed.

Figures 12–14 show the effect of the stack gas final temperature on the calculated opacities. Upon cooling the stack gases from the assumed initial temperature of 300°C, the opacity is essentially zero until the sulfuric acid dewpoint is reached. The mass concentration and size of the nuclei are such that the opacity is less than 1%. At the acid dewpoint the opacity increases substantially for the higher $H_2SO_4$ concentrations (20 and 70 ppm) and gradually for the lower $H_2SO_4$ amount (5 ppm). At the 70 ppm initial $H_2SO_4$ the calculated opacities increase greatly upon cooling below the sulfuric acid dewpoint such that no significant increase in the opacity occurs with cooling past the water vapor dewpoint. At the 5 ppm initial $H_2SO_4$ concentration the calculated opacities increase somewhat upon cooling past the acid dewpoint and then increase substantially after cooling below the water dewpoint.

The results reported in Figs 12–14 can be compared to the measured opacities reported by Nader and Conner (1978) for an oil-fired boiler. The measured opacities were reported to be about 20% at instack conditions (160°C and around 8 ppm $H_2SO_4$) and 40% outside the stack. The opacity was measured instack with a light transmissometer and outstack with Lidar and human observers. Assuming the 20% instack opacity was entirely due to the solid particles (carbon and fly ash), the increase in opacity from the 20% instack to the 40% outstack appears in general to be similar to the increases shown in the calculated opacities in Figs 12–14 for the cooling of gases from 150°C to the lower temperatures.

## 7. CONCLUSIONS

The calculated opacities, based on light extinction theory and sulfuric acid condensation data, show that for the conditions considered and at stack gas temperatures in excess of 125°C, initial $H_2SO_4$ stack gas concentrations of 10 ppm or less will result in calculated opacities of 20% or less for a 6-m stack diameter. The calculations also illustrate that the final acid droplet diameters and opacities are significantly affected by both the initial $H_2O$ vapor concentration and the initial $H_2SO_4$ concentration. The equations and calculation procedures presented are of significance to explaining the plume opacities observed for emissions containing sulfuric acid.

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